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XXVII. *The Effect of Tension on certain Elastic Properties of Wires.* *By* E. EDWARDS, *M.A.*, *B.Sc.*, I. BOWEN, *M.Sc.*, *and* S. ALTY, *M.Sc.**

[Plate VII.]

AN increase in the torsional stiffness of phosphor-bronze strips as the result of increased tensions was investigated by Pealing †. In the experiments to be described the phenomenon was further examined with the view to seeing, if possible, the nature of the mechanism involved. In the first part of the work the dynamical method was applied, and considerably more light was thrown on the effect. The variation of stiffness was found to be present in all the wires tested, although the amount of change depended on the crystalline condition of the material. An investigation of the amount of damping for torsional vibrations established the additional fact that it was reduced as tension was increased. A statical method was then evolved in which observations could be obtained more readily and with greater accuracy. This was applied to test-materials which were considered to possess a simpler internal structure—tungsten wire consisting of a single crystal in the first instance, and quartz filament, presumably non-crystalline, in the second instance.

These experiments seemed to show that the phenomenon depended on the structure of the material being partly crystalline and partly amorphous.

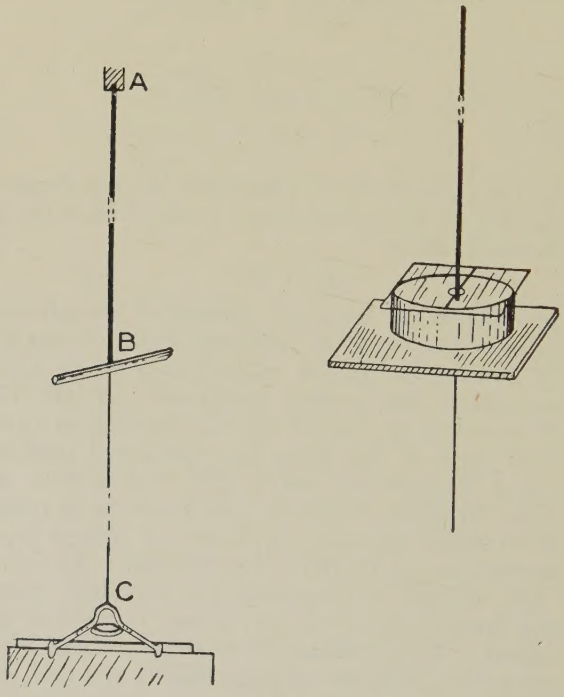
* Communicated by Prof. L. R. Wilberforce, M.A.

† Pealing, Phil. Mag. (ser. 6) vol. xxv. no. 147 (March 1913).

Dynamical Observations by I. Bowen, M.Sc., sometime Oliver Lodge Fellow.

Before proceeding on fresh lines the work of Pealing * was in part repeated, and the curves he obtained verified. His experiments had been performed by observing the oscillations of suspended bars of varying mass and inertia, and so calculating the torsional stiffness of the suspending phosphor-bronze strip for each case.

Fig. 1.



In the first part of the work recorded here, the change in moment of inertia of the suspended system was eliminated by use of the apparatus shown in fig. 1.

An oscillating bar B having moment of inertia large enough to give easily measurable period, but having small mass, was soldered to the end of a phosphor-bronze test strip AB, whose dimensions are given in the table of

* *Loc. cit.*

observations. From the point of suspension of this horizontal bar hung a fine unspun silk fibre BC, which could carry loads up to about 60 grms. The upper end A of the test strip or filament was clamped firmly in a vice, and to the end C of the silk fibre was attached a very light aluminium scale-pan. The masses of the inertia bar B and scale-pan C were kept small so that the suspension could be tested under a tension as small as 0·7 grm.

In earlier experiments a vane consisting of a weighted metal box which just floated in glycerine (at a depth sufficient to leave only an attached scale-pan unimmersed) was used to prevent any rotation of the scale-pan ; and the silk fibre BC was ascertained to have torsional stiffness small enough not to affect appreciably the period of oscillation of the strip and inertia bar AB.

A load varying from 0·7 to 60 grms. could thus be applied to the test strip AB and its period of oscillation determined, while the inertia of the system remained constant.

In later experiments the vane and glycerine were for convenience replaced by an aluminium scale-pan bearing two rigid projecting arms which hung between two vertical glass plates whose distance apart allowed the minimum of freedom to the arms.

This arrangement, as seen in fig. 1, allowed no rotation of the scale-pan, and at the same time the absence of friction at the glass surfaces permitted of the total load being applied to the test strip.

The results of experiments with this apparatus are expressed by the typical Curves I, where ordinates give $\frac{1}{T^2}$, T being the period of oscillation of the phosphor-bronze strip of length about 25 cm., breadth 0·054 cm., and thickness 0·0035 cm., and are proportional to the rigidity ; while abscissæ give the tensions of the suspending strip measured in grammes. It will be seen that the torsional stiffness of the suspension increases with the load until at a certain value the rigidity becomes constant, and remains constant as the load is further increased.

In order to vary the conditions of the experiment, the silk fibre and scale-pan were replaced by a set of inertia bars of different moments of inertia and masses. Two pairs of bars were of equal mass but widely different inertia. Bars 5, 6 and 7, 8 form two such pairs. Thus taking one pair, the period of oscillation on a given suspension would be different for the two members ; while their equal masses would cause the torsional stiffness of the suspension to be the same for

both, provided the stiffness was dependent on tension alone, and not on period of oscillation. Results showed that the torsional stiffness depended only on the load applied.

The masses and moments of inertia of the bars are given in Table A below, with corresponding observations on the period. Curve II is derived from this table.

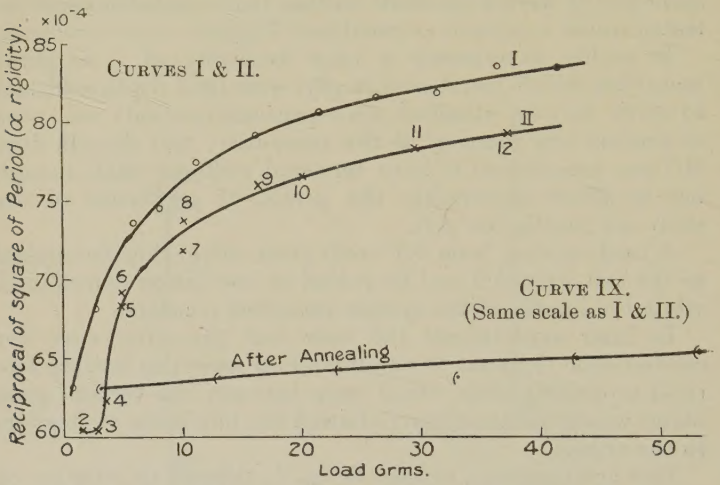


Table A.—Phosphor-Bronze Strip as Suspension.

Length 29·2 cm. Breadth 0·054 cm. Thickness 0·0035 cm.

The weight and moment of the wire cradle supporting the bars are included in the figures given in the second and third columns respectively.

Bar.	Tension, grms.	Moment of Inertia, grm./cm.²	Period of Swing.	Torsional Stiffness.
1	0·625	4·30	4·90	7·02
2	1·43	8·72	7·41	6·23
3	2·76	22·00	11·8	6·23
4	3·49	48·85	17·4	6·35
5	4·90	150·32	29·6	6·76
6	4·90	13·17	8·70	6·81
7	10·20	72·25	20·2	7·00
8	10·29	136·19	27·5	7·13
9	16·09	295·4	40·0	7·29
10	19·65	259·0	37·4	7·33
11	28·65	254·3	36·6	7·47
12	36·77	545·6	53·4	7·55

The loads were not quite large enough to reach the horizontal part of the curve.

The fifth column in the above table gives values of the

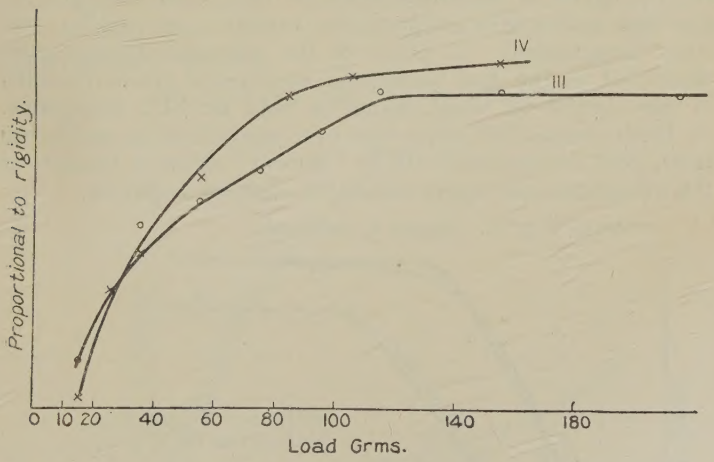
torsional stiffness τ of the suspension, τ being related to the period of oscillation T by the equation

$$T = 2\pi\sqrt{\frac{I}{\tau}},$$

where I is the moment of inertia of the suspended system about the axis of swing. It will be seen that the curve resembles those obtained by the previous method, and demonstrates the independence of τ and T since for bars of equal mass the values of τ are approximately equal, although the moments of inertia vary greatly.

In his researches Pealing failed to discover a variation of rigidity in wires having circular cross-section, and was led by this amongst other reasons to regard the variation in strips as being not a true change in rigidity but a change in torsional stiffness due to the effect of rolling in manufacture.

Curves III & IV.



The search for the effect in phosphor-bronze wires (the term "wire" being used here to imply circular section) was therefore of importance, since a wire drawn through a die-plate receives equal treatment over all parts of its surface; while the rolling of strips might overstrain one side of the material more than the other, in the manner suggested by Pealing. In other words, evidence of the variation in wires would lend support to the view that the phenomenon is not anomalous, but a true variation of rigidity.

The variation was found by the writer in phosphor-bronze wires, the specimens being supplied by Messrs. Johnson & Matthey. Curve III is drawn from a series of observations

on the wire by the use of a scale-pan and glass plates described earlier in this paper. The maximum load applied in this case was 200 grms.

(It might be well to state here that decreasing loads were tried in these experiments, and the curves would always repeat themselves ; in fact this procedure was always used as a proof that suspensions had not suffered overstrain under the maximum tension.)

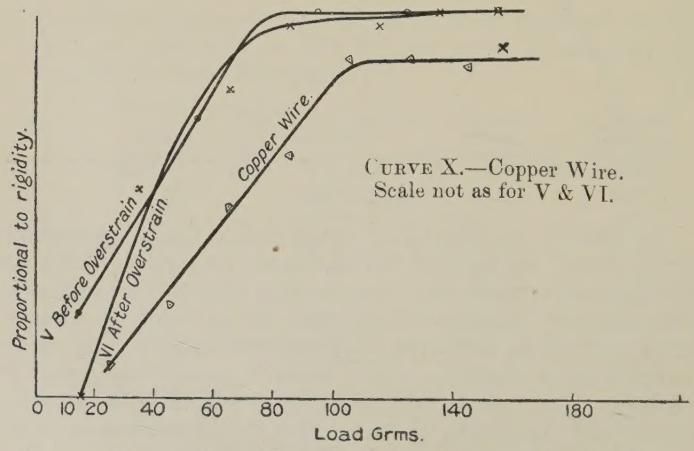
The period of 400 complete oscillations was determined to give each value.

Curve IV represents a series of readings on another piece of wire.

It is justifiable to assume that the shape of cross-section is not a determining factor of the presence of variation in torsional stiffness, for the curves give the same evidence of maximum rigidity as before. The wire had a diameter of 0·04 cm. and length about 35 cm.

The effect of overstrain, which had been thought by previous workers to produce the variation in rigidity, was next ascertained. A piece of the phosphor-bronze wire described in the last paragraph was loaded gradually until it was found to break under a load of 11·2 kilograms. A fresh unstrained piece was now submitted to oscillation tests, then overstrained till it "flowed" under a tension of 9·6 kilograms, and again tested for rigidity variation.

Curves V & VI. Drawn to same scale.

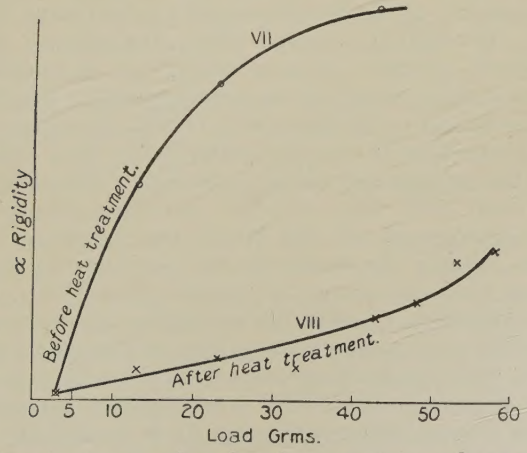


Curves V and VI show the variation in rigidity before and after overstrain. The variation is still present, and the turning-point of the curves occurs for the same value of

tension, roughly 100 grms. The variation does not disappear when the material is overstrained.

In order to examine the effect of heat treatment on the rigidity variation, a furnace was built of a glazed porcelain tube measuring 30 cm. in length and having an internal diameter of 3 cm. Around this tube was wound a solenoid of nickel-chromium alloy resistance-wire capable of giving a temperature of 2000° C. with a current of 7 amps. The windings were about 2 mm. apart, being closer at the ends where cooling might be considerable. The whole was enclosed in a plaster of alundum powder mixed with sodium silicate and wrapped with asbestos cord and sheeting to form a thick coating. A small vice at one end of the tube held one end of the wire undergoing treatment, the other end being held taut outside the surface by a weak spiral spring. Since phosphor-bronze oxidized rather readily at high temperatures, a copious supply of hydrogen was kept flowing through the furnace. A platinum resistance thermometer in conjunction with a Callendar-Griffiths bridge gave temperature readings.

Curves VII & VIII. Drawn to same scale.



For 30 minutes a phosphor-bronze strip, whose rigidity had been examined in the usual way, was maintained in the furnace at a temperature of 350° C. After slow cooling, the part of the strip which had been inside the furnace was again tested. The material had become soft and less springy, indicating that annealing had taken place to some extent. The results of the tests before and after heating are given by Curves VII and VIII.

There appeared a decrease in the rigidity variation amounting to about 70 per cent., while after heat treatment no turning-point, at which rigidity ceases to increase with load, was apparent, even though the load applied reached 60 grms.; whereas before heating a turning-point occurred between 20 and 30 grms. Several strips were examined after heating to 400° C., and the variation in torsional stiffness was always present though much reduced.

Microscopic examination of the effects of heat treatment on the metal was next attempted. Specimens 1·5 cm. in length were mounted in sealing-wax and polished, with a polish-etch of magnesium oxide in ammonia to which had been added a few drops of hydrogen peroxide. The difficulties of handling such fine specimens need not be described here. Photographs of specimens so prepared taken under "normal illumination" are shown in Plate VII. In the unheated specimens of phosphor-bronze the crystals were seen to be much elongated due to cold rolling in the manufacturing process. The crystals were all of the same composition, a solid solution or binary alloy of the two constituent metals which had remained unchanged by the process of solidification.

Examination of the specimen which gave Curve VIII after heating to 350° C. showed the development of small "incipient" crystals as new centres of recrystallization. To obtain more complete recrystallization a length of the strip was heated in the furnace to 730° C. and maintained so for an hour, when it was slowly allowed to cool. A rigidity test on this specimen yielded Curve IX. The variation was still present after this complete annealing (shown by the second photograph on the plate) and formation of large crystals. Again the curve showed no turning-point corresponding to the attainment of a maximum rigidity.

Thus annealing lessened the variation, the decrease being greatest for most complete annealing, or formation of largest crystals, while the turning-point disappears from the curves.

Lack of time prevented the working of a complete set of data for drawn copper wire, but it is noteworthy that the same variation and turning-point was discovered in copper. Curve X shows the variation in rigidity of a drawn copper wire 0·033 cm. in diameter.

Partial annealing was again found to lessen the variation. The experiments so far described led to the idea that the variation in rigidity was caused by some internal mechanism in the crystals of the metal. The simplest explanation seemed to be that of slip within the crystals. Should a crystal be

deformed by slip along a slip-plane, then, provided the deformation be slight, any disturbed molecules in the plane of slip would be able to rearrange themselves pretty much in their original way, crystal orientations and integrity being thus restored. Excessive slip would produce permanent disturbance in a slip-plane, while excessive alternating strains tend to produce an amorphous layer in the slip-plane, giving rise to "fatigue" *.

In the experiments described here, the deformation was slight enough to permit of rearrangement of the disturbed molecules. The individual crystals of a metal are, according to Rosenhain, surrounded by an intercrystalline cement of amorphous metal, and recent work goes to show that this amorphous metal possesses greater strength than the crystal itself, slip-bands occurring in such a way as to produce least disturbance of this cement.

Thus in a strip of phosphor-bronze we have a large number of crystals bound together by a three-dimensional network of strong amorphous metal. When the strip or wire is under tension, the intercrystalline cement binds tightly on the crystals and prevents their internal slipping; while under sufficient tension this binding effect may be great enough to prevent any slip in the crystal, rigidity then remaining constant in spite of further increase in tension.

When crystals are small, as before heat-treatment, the binding effect of the amorphous cement is more pronounced and the maximum rigidity is reached for a smaller load than is necessary when crystals are large. This would account for the absence of a turning-point in the rigidity curves for annealed specimens.

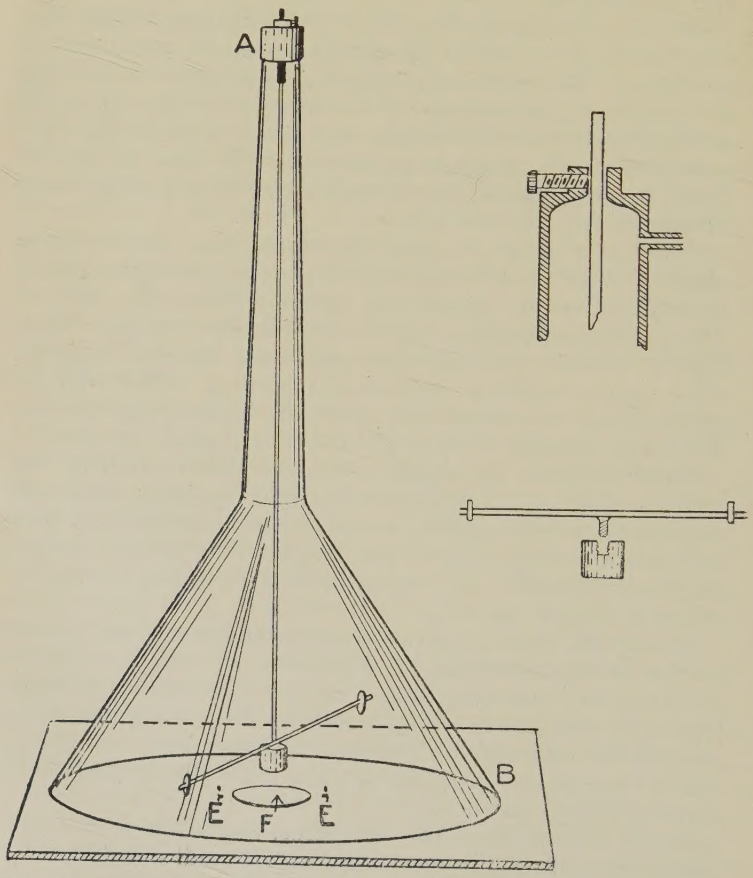
To test this theory a series of experiments was carried out on the internal damping of oscillations in phosphor-bronze suspensions. Damping should be great when internal slip is great; while the damping would reach a minimum when slip ceased and rigidity became maximum and unvarying, that is to say, for large loads. The following experiments bore out this prediction.

In fig. 2 is sketched the apparatus, consisting of a large filter funnel ground to fit closely on to a stout metal base B. On the small end A of the funnel was fitted a cap having an exhausting tube and a clamp which allowed a stout rod to pass through (as shown in the smaller diagram). To the lower end of this rod was soldered the phosphor-bronze suspension. In these damping experiments it was desirable

* Ewing and Humphrey, Phil. Trans. Roy. Soc. A, cc. (1902).

to keep the period of swing constant, and so overcome variations due to air-friction. The different loads applied were therefore constructed to have equal moments of inertia, and to screw on to the light inertia bar as in fig. 2. Any slight inequality in moment of inertia could be compensated by adjusting the positions of the two small iron disks on the

Fig. 2.



inertia bar, while the suspended system could be set oscillating by means of an electromagnet held outside the chamber to attract either of these disks. The apparatus was exhausted to reduce variation due to air-friction or viscosity when the different shaped loads were applied.

A removable plug F in the base-plate facilitated the changing of the loads, small hooks E in the base serving to hold the inertia bar steady during the operation.

The sliding bar in the cap A permitted the lowering of the suspension for changing the load. All joints were made air-tight with wax. A scale penned on the glass wall of the funnel at its base gave amplitude readings.

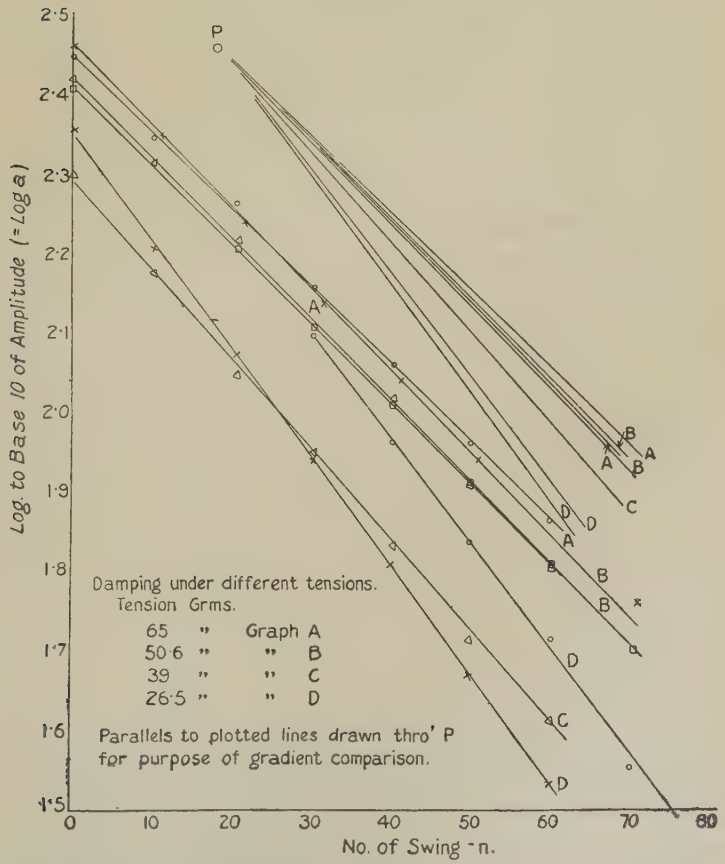
If r be the ratio of two successive amplitudes to one side, and a_0, a_1, a_2, . . . a_n the amplitudes of the 1st, 2nd, 3rd and (nth + 1) swings to the same side, then

$$r^n = a_0/a_n$$

and

$$\log r = \frac{\log a_0 - \log a_n}{n}.$$

Graphs XI.


Log. to Base 10 of Amplitude (= Log a)
No. of Swing = n.
Damping under different tensions.
Tension Grms.
65 " Graph A
50·6 " " B
39 " " C
26·5 " " D
Parallels to plotted lines drawn thro' P
for purpose of gradient comparison.
P

Thus if the damping has been uniform through a set of oscillations, a graph giving values of n as abscissæ and corresponding values of log a_n as ordinates should be a straight line, as shown by graphs XI. Each line

in this set was obtained as the result of several damping tests for a particular load. It is clearly seen that the coefficient of damping decreases as tension and rigidity increase, while there is a limit to the damping as there is to rigidity, both limits occurring for about the same value of tension. These experiments on damping therefore support the theory suggested to explain the variation in rigidity.

Statical Measurements by S. Alty, M.Sc.

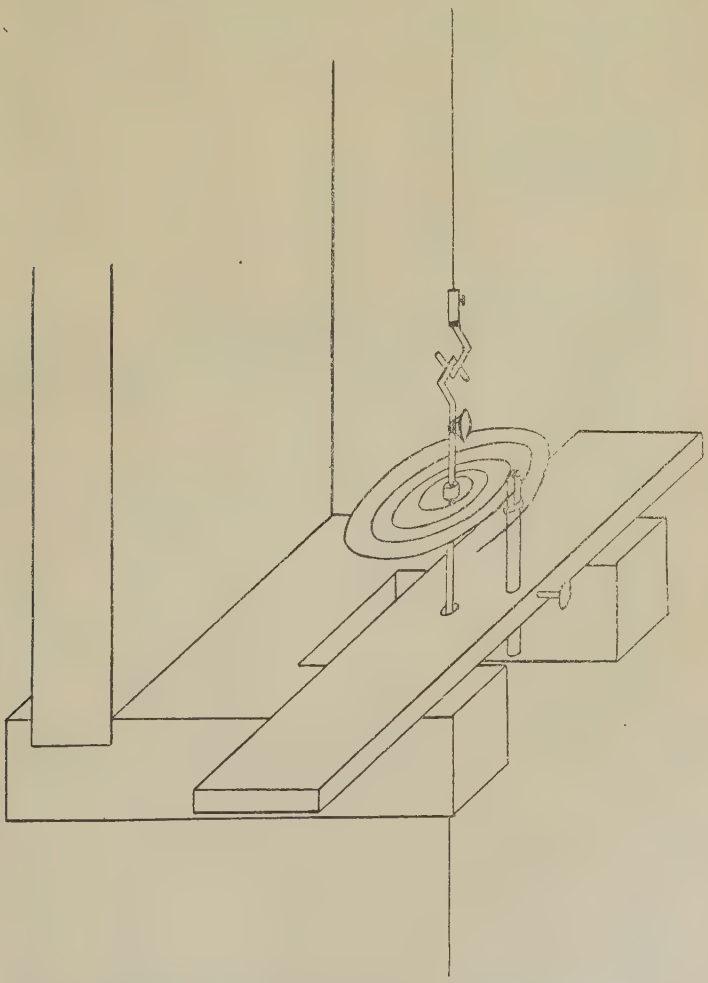
Experiments of a statical nature were carried out to investigate further the variation of stiffness of strips and wires with load. The method and apparatus used were somewhat similar to those described in Searle's 'Experimental Elasticity,' p. 155, in connexion with torsional hysteresis.

The upper end of the wire was clamped to a torsion-head graduated to read tenths of degrees, and the lower end was attached to a flat spiral spring of suitable strength, the outer end of this spring being clamped to the framework. Changes in the strength of this spring were easily made by altering the part of the spring engaged in the framework-clamp, and so varying the length of the spring. As can be seen in fig. 1 *a*, the attachment to the spiral spring is made through two hooks of square cross-section to provide geometrical contact for the transmission of couples. This provision made the substitution of wires an easy matter. The tension is governed by the weight which is attached below the stand. The method of procedure was to produce a twist of known amount by the torsion-head, causing the lower end to turn through a small angle in opposition to the controlling spring. This angle of rotation was measured by means of a mirror fixed to the central wire. The couple acting was proportional to this angle. Hence we got a measure of the couple corresponding to any twist produced.

As the tensions were produced by attaching weights to the wire below the spiral spring, a complication entered due to the rotation of the wire at its lower end. If the scale-pan carrying the weights was free, then this rotation when produced caused the scale-pan to vibrate torsionally, and this vibration would upset the reading obtained from the mirror. There were two ways of overcoming this difficulty in theory. The first would be to prevent any rotation of the scale-pan and to interpose some very fine suspension between the spiral spring and the scale-pan to eliminate any controlling effect on the twist of the spiral spring and wire. At best, this would leave a slight residual controlling effect and the

reading obtained for the twist of the lower end of the wire would be slightly reduced on that account.

Fig. 1 *a*.



The way adopted, therefore, was to turn the scale-pan by hand through an angle equal to the rotation of the wire at the spiral spring. In this way the twist in the suspension from spring to pan was maintained zero. This method worked very satisfactorily.

The order of procedure in an experiment was as follows :—

The wire was attached to the torsion-head, spiral spring, and scale-pan. All control was removed by unclamping the

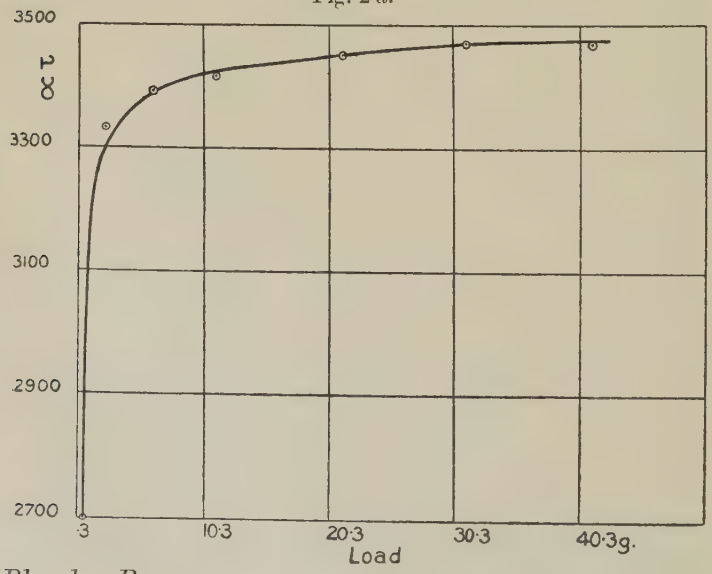
framework end of the hair-spring and allowing the scale-pan to be quite free. The mirror readings at spiral spring and scale-pan were noted, the outer end of spring was now clamped, the torsion-head was turned through an angle $\theta_1°$, and the deflexion $\theta_2°$ for the lower end observed on the scale. The scale-pan was then turned through an angle equal to this, or rather slightly more because, as the scale-pan is turned, θ_2 increases slightly.

Then the total twist in the wire $= \theta_1 - \theta_2$, and the couple G is proportional to θ_2.

$\frac{G}{\theta}$, which measures the stiffness, is therefore proportional to $\frac{\theta_2}{\theta_1 - \theta_2}$.

Measurements were made of these angles for a series of loads for each wire or strip tried, using in each case various values of angles. The results were shown graphically by plotting the value of θ_2 against the corresponding value of $\theta_1 - \theta_2$.

Fig. 2 *a*.



Phosphor Bronze.

With phosphor-bronze strips, the first material to be tried, a variation in the stiffness of the same general character was obtained with all, but the amount of the change varied from 5 per cent. to 35 per cent. in different specimens.

The curve shown in fig. 2 *a* is typical of the effect obtained

These results agreed in a general way with those that had been obtained by the dynamical method of Mr. Bowen.

As the phenomenon had already been shown to be connected with the internal structure of the metal, it was desirable to test specimens of known internal structure, and possibly, in that way, gain some knowledge of the mechanism involved.

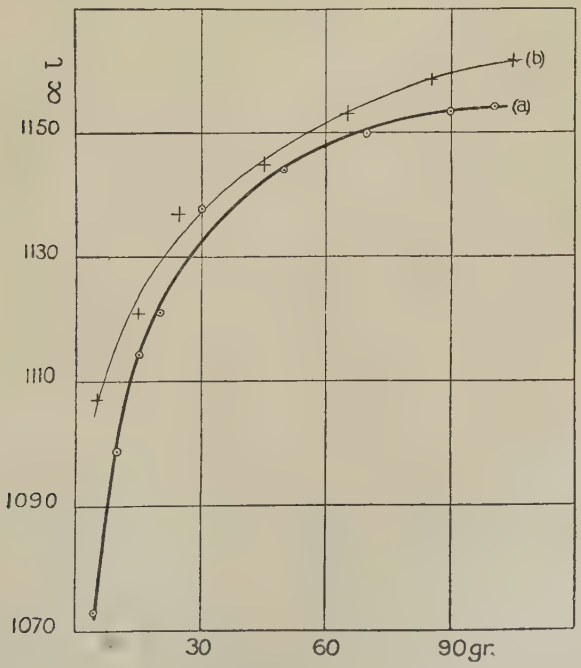
Tungsten.

Through the kindness of the General Electric Company, lengths of tungsten wire and of Pintsch single crystal wire were obtained and tested by the above method.

The diameter of the wire was ·20 mm.

The hair-spring used for the phosphor-bronze strips was replaced by a much stronger one, and the effect due to the stiffness of the thread between spiral spring and scale-pan became inappreciable. In all other respects the apparatus was unaltered.

Fig. 3 *a*.

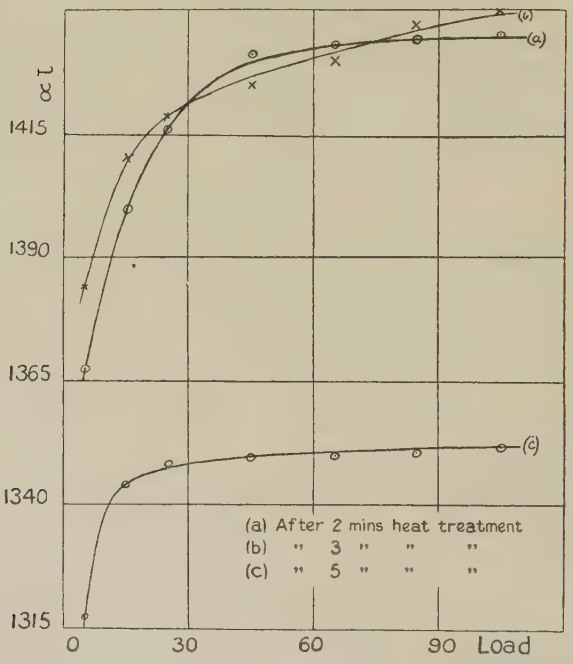


The results of the experiment on the ordinary drawn tungsten wire are shown in fig. 3 *a*, curve (*a*), the curve being of the usual type and the percentage increase in stiffness being 7·46 per cent. between loads of 5 and 105 g.

In the drawn wire there will be a large number of crystals occupying any one cross-section. The Research Staff of the G.E.C. have carried out experiments * on the properties of "recrystallized" tungsten wire. In this the crystals will have grown, and if the recrystallization is complete then many of the crystals will fill completely the cross-section of the wire.

With the view to finding how the change of stiffness varied with the size of the crystals, the stiffness experiment was carried out on the ordinary drawn wire at stages of increasing recrystallization.

Fig. 4 *a*.

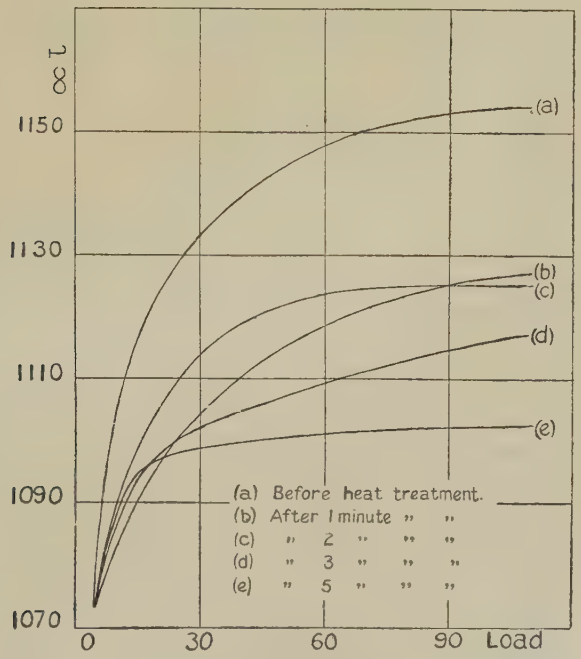


As the recrystallized wire was extremely brittle, it was necessary to carry out the process *in situ*. To do this the wire and the hook attached to it were enclosed in a glass tube fitting on to a stopper which was attached to the torsion-head. The hook supported a small cup of mercury, this giving good electrical contact, and exerting sufficient tension on the wire to hold it taut. Recrystallization was brought about by raising the wire to a white heat in an

* Phil. Mag. Aug. & Nov. 1924.

atmosphere of hydrogen, the current necessary being led in by mercury connexions and a platinum contact at the bottom of the tube. The current was passed through the wire for one minute, the tube removed, the spring hook replaced on the other, and the experiment repeated. This was done four times on the supposition that the crystals would become larger each time, and the results are shown in figs. 3 *a*, 4 *a*, and 5 *a*, the change in stiffness becoming less. In fig. 5 *a*

Fig. 5 *a*.



the curves for the wire in all its stages are given the same value of stiffness for a load of 5 g., and the scale of each curve suitably reduced for ease of comparison.

The Pintsch tungsten wire, which consisted entirely of a single crystal, was next tested and was found to show no variation, the torsional stiffness being independent of the load. The largest discrepancy was less than 1 per cent., and was considered to be due to the fact that for loads of less than 10 g. the wire was not taut. There was no indication of a regular variation with load.

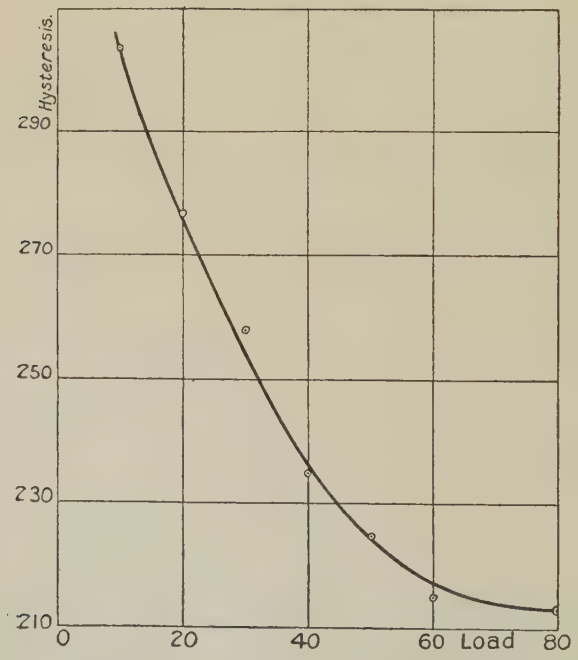
Quartz Fibre.

The experiment was also carried out using a quartz fibre, this having no crystalline structure, and it was found that the stiffness was quite independent of the load.

Variation of Hysteresis of Wires with Load.

On carrying out the usual hysteresis experiments for the drawn tungsten wire, it was found that the hysteresis loop was too narrow and indistinct to be of use in showing in what way, if any, the amount of hysteresis varied with load. An indication of the hysteresis for different loads was found as follows :—With the wire originally free from twist, the torsion-head was turned through 360° in a clockwise direction

Fig. 6 *a*.



and then back to zero. The spot of light reflected from the mirror attached to the hair-spring was observed to have been deflected in a counter-clockwise direction, and its new position was noted. On turning the head through 360° in a counter-clockwise direction and back to zero the spot of light shifted in the opposite direction, and its reading was

again observed. The difference between the two readings was proportional to the amount of slip which had occurred in the wire during the two twists. The difference between these readings may be taken as an indication of the amount of hysteresis.

It was necessary to bring back the torsion-head accurately to zero, since a small error here would have rendered the scale-readings useless. To do this a mirror was attached to the head and a scale set up at a distance of 1 m. from the mirror. The torsion-head was turned so that the spot of light returned to the same point on this scale each time, thus ensuring that the head was always brought to the same zero. In this way a measure of the hysteresis was obtained for a series of loads.

The Pintsch single crystal wire showed practically no variation of hysteresis with load, there being slight irregularities for loads less than 10 g. due probably to the fact that the wire was not taut. For loads above 10 g. the hysteresis was constant.

The results obtained for the drawn tungsten wire are shown in fig. 6 *a*. In this case the hysteresis varies greatly with load, assuming a minimum value at a load of about 75 g., and remaining unchanged for loads of higher values

The Young's Modulus of Wires for Small Tension.

In view of the general variation of torsional stiffness, it was considered desirable to examine the stretching of wires by small tensions. The great difficulty in this investigation was to ensure the absence of spurious effects due to the straightening out of small irregularities. When this had been overcome, it was observed that the ratio of increase of length to the stretching force was much greater for the smallest forces employed than for larger ones. This has been observed with copper and iron wires of about 1 mm. diameter, the change disappearing for tensions of the order of 100 grms. The work has not proceeded far enough for publication at present, but it is hoped that the results for a number of different materials together with an account of the method and apparatus employed will be completed shortly.

Conclusions.

One fact seems to be well established—that the observed changes in the elastic properties of materials depends on their structure being partly amorphous and partly crystalline,

and that they are most marked when the crystals are small, a condition produced by any hardening process. From the elementary theory, it can be seen that the stress due to a tension may be regarded as equivalent to a hydrostatic negative pressure (an outward pull on all parts of a surface) together with two shearing stresses in two perpendicular planes, both of which pass through the axis of the wire. Of these, it seems reasonable to consider the first as responsible for the observed effect, in so far as it involves a change in volume of any element, which implies an increase in the separation of the molecules.

The condition seems to be analogous to a chain composed of a large number of links, but in our case we have a network of links, in three dimensions; under small tensions there is a looseness in the linking together of neighbouring elements, while increase of tension by separating these elements slightly, increases the strength of the bonds existing between them.

Other experiments have shown that slip occurs readily in crystals along certain planes. The fact that a wire of one crystal does not exhibit any variation, tends to lead to the view that the crystals in the interior of a multicrystalline material are not in the same condition as would be found in the case of a single large crystal. This difference must be caused by the intercrystalline amorphous material or cement as it is commonly called. A hydrostatic pressure on the crystals might conceivably account for the effect, provided such a pressure resulted in greater freedom of slip within the crystals, and an experiment to test this point is being contemplated. If that could be established as a fact, the mechanism involved in the increase of stiffness and decrease of damping and hysteresis would be fairly clear. The increase in volume brought about would relieve the pressure on the crystals, and they would exhibit properties similar to those of single large crystals with free surfaces.

In conclusion, the authors wish to express their thanks to Prof. L. R. Wilberforce for suggesting the work, to Prof. C. O. Bannister for placing the resources of the Metallurgy Department both as regards equipment and advice at our disposal for getting the photo-micrographs, and to the General Electric Company for their kindness in allowing us to have a length of their single crystal tungsten wire.

XXVIII. *The Surface Tension of Liquid Metals.*—Part I. *Tin and Lead.* *By* L. L. Bircumshaw, *B.A., M.Sc.* (*from the National Physical Laboratory*) *.

THE surface tension of molten metals was the subject of experimental study by Quincke † as long ago as 1868. In this paper and in one ‡ which appeared in the following year, determinations of this constant were made by a somewhat crude application of the drop-weight method, viz. the weight of the drops which fell from a melting wire of known diameter was determined. The difficulty of controlling the formation of the drops and the great uncertainty of the circumference from which the drop falls render this method little more than qualitative. In later papers § by the same author the capillary constants were deduced from measurements of the dimensions of a drop of the molten metal resting on a plane surface. Siedentopf ‖ in 1897 published a paper containing the results of a large number of determinations by this method, and it has also been used by Heydweiller ¶ and by Gradenwitz **, while Grünmach †† used the method of ripples. Smith ‡‡ measured the capillary depression of the metal in a carbon tube, using a micrometer depth gauge and an electrical device, and gives results for mercury (15°–17°), bismuth (700°–850°), antimony (840°–850°), lead (770°–780°), tin (750°–910°) aluminium (700°–820°), zinc (580°–630°), silver (980°–1120°), gold (1120°), and copper (1150°). In this work, however, the angle of contact was assumed to approach 180°, so that in all probability most of these results will be low.

The most important work on this subject during recent years is due to Hogness §§, who used the method of "maximum bubble pressure." He measured the excess pressure developed in a small bubble of the metal when forced from the end of a fused silica tube of known radius, and determined in this manner the surface tension of mercury (up to

* Communicated by Walter Rosenhain, B.A., D.Sc., F.R.S.
† Poggendorf's *Annalen*, cxxxiv. p. 356 (1868).
‡ Poggendorf's *Annalen*, cxxxv. p. 261 (1869).
§ Poggendorf's *Annalen*, cxxxviii. p. 141 (1870); cxxxix. p. 1 (1871).
‖ *Ann. d. Physik*, lxi. p. 235 (1897).
¶ *Ann. d. Physik*, lxii. p. 694 (1897); lxv. p. 311 (1898).
** *Ann. d. Physik*, lxvii. p. 467 (1899).
†† *Ann. d. Physik*, iii. p. 660 (1900).
‡‡ Journ. Inst. Met. xii. p. 168 (1914).
§§ Journ. Amer. Chem. Soc. xliii. p. 1621 (1921).

the boiling-point) and of tin, lead, bismuth, cadmium, and zinc up to 500°. The theory of the method of maximum bubble pressure was first described by Cantor *, and subsequently by Feustel †, Ferguson ‡, and Schroedinger §, who gives the formula

$$a^2 = rh\left(1 - \frac{2}{3}\frac{r}{h} - \frac{1}{6}\frac{r^2}{h^2}\right).$$

Here a^2 is the specific cohesion, r the radius of the tube, and h is the maximum pressure in the bubble expressed in centimetres of the liquid itself. This formula obviously only holds when $\frac{r}{h}$ is small, but a complete numerical solution of the differential equations involved is given by Bashforth and Adams ‖. Sugden¶ in a valuable paper has dealt with the theory of this method and utilized Bashforth and Adams's tables to calculate values of the complete correction $\frac{X}{r}$ in the equation $a^2 = rh \cdot \frac{X}{r}$, and gives a table of values of $\frac{X}{r}$ for a range of $\frac{r}{a}$ from 0·0 to 1·5. In the present work it was decided to use the method of maximum bubble pressure, as it possesses two great advantages: it is independent of the angle of contact, values of which in the case of liquid metals are almost always unknown, and a new surface of the metal is blown in each separate determination.

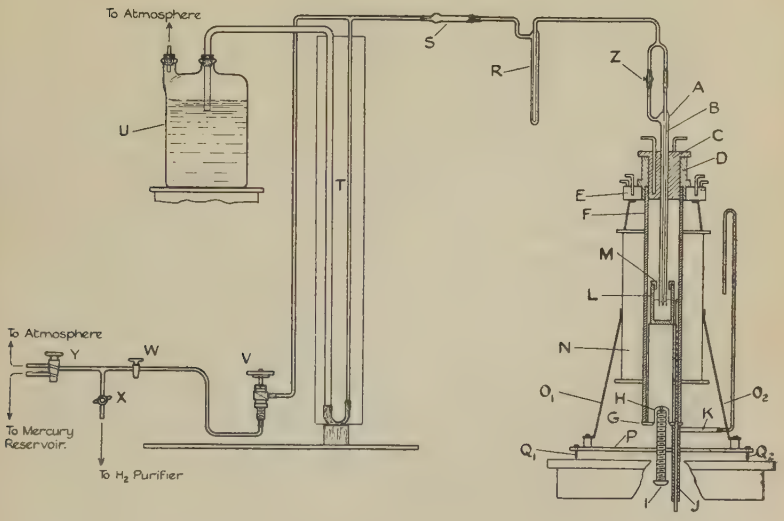
Experimental.

The apparatus is shown diagramatically in fig. 1, and consists of a fused silica tube A, 42 cm. long, 1·12 cm. external diameter, and 0·92 cm. internal diameter, into which is fused a second silica tube B about 0·4 cm. diameter. This tube has been drawn down and the ends of both tubes have been ground, so that the cross-section of each is in the same plane. The diameter of the tube has been measured in two directions at right angles in the Metrology Department of the National Physical Laboratory, and the measurements were found to differ by 1 per cent., the mean diameter

* Wied. *Annalen*, xlvii. p. 399 (1892).
† Drud. *Annalen*, xvi. p. 6 (1905).
‡ Phil. Mag. vi. p. 128 (1914).
§ *Ann. d. Physik*, xlvi. p. 413 (1915).
‖ 'Capillary Action,' Cambridge, 1883.
¶ Trans. Chem. Soc. cxxi. p. 858 (1922).

being 1·016 cm. The tube A fits closely through a hollow water-cooled brass plug C, which in turn fits into the brass collar D; E is a copper water-cooler placed in close contact with the lower half of the latter. The silica furnace tube F at its lower end is closed by a brass plate G fitted with a central cone H, into which passes the screw I, and soldered into this plate is a brass tube J, through which passes the silica couple tube. Another brass tube K is soldered into J, to the end of which is attached a glass tube (2–3 mm. in diameter) which serves as a gas outlet from the furnace.

Fig. 1.



On the plate G rests a Mabor cylinder, which supports an alundum crucible L which contains the metal, and a clay cover M fits the top of the crucible. The furnace-tube is wound with nichrome wire and the case N is held by three steel stays O_1 O_2 O_3, which are screwed down to the base P, the latter being supported on the table by three levelling screws Q_1 Q_2 Q_3. After the tube A had been fitted through the plug C and held firmly in position by means of a little pitch on the top surface of the plug (a film of wax was also placed between A and the inside wall of the cooler), the lower ends of the two tubes were very carefully ground so that their cross-section lay in the same plane, and this plane was parallel to the machined top of C. In order to ensure

that the plane of cross-section of the tubes is horizontal, it is then only necessary to level up the top of C with a spirit-level, by means of the screws Q_1, etc. The joint between the furnace-tube and the plate G is made tight with a little clay, which is covered with a film of pitch. This has been found to be quite satisfactory. The tubes A and B are connected by means of pressure tubing, in the manner shown in the sketch, to a glass trap R immersed in solid CO_2 and acetone contained in a thermos flask, and the trap is connected through a drying tube S (loosely packed with calcium chloride) to the manometer T. One arm of the latter consists of a narrow tube 50 cm. long and 3 mm. diameter graduated in millimetres, which was carefully calibrated before being sealed into the apparatus. The wide arm is connected to a large Woolf bottle U 16 cm. in diameter and is open to the atmosphere. Water, coloured with a trace of potassium dichromate, was used as the manometric liquid, and no trouble due to the sticking of the meniscus was observed. The manometer is also connected through a valve V to the taps W, X, and Y.

To make a determination, a piece of metal of about the correct volume is turned up to fit loosely into the crucible and a cylindrical hollow cut in it, into which fits very loosely the end of the tube A. The joint at G is sealed and the junction between the plug C and the collar D waxed over. Hydrogen, generated electrolytically from 5 per cent. caustic soda (using iron electrodes), is passed over silica chips heated to 600° and dried over calcium chloride. The gas is then passed through the apparatus for two to three hours by closing Y and opening X and W, after which the furnace is heated until it has attained the desired constant temperature. Attached to the tap Y is a large gas burette, and by closing W this can be filled with gas from the generator, then by opening Y and W and closing X, bubbles can be blown by using the gas in the burette under a convenient pressure. The valve V enables the bubbles to be formed quite slowly. A determination consists in measuring the pressure required to liberate a bubble from the wide tube and the pressure required to liberate a bubble from the narrow tube, and from these observations the surface tension can be calculated. A screw clip is placed on the connecting rubber tubing at Z, and if this is open bubbles will blow from the wide tube, whereas if it is closed they will, of course, come from the narrow tube. When bubbles are blown from the latter, the pressure

rises and the metal is depressed in the wide tube, which alters the hydrostatic head slightly. After each reading with the narrow tube therefore the pressure in the apparatus is carefully released (nearly to atmospheric) through the tap Y. After a determination when the metal is just above the melting-point, the seal at G is broken, and by means of the screw I the metal before it freezes is dropped just below the end of the tube A.

The results are calculated by the method given by Sugden (*loc. cit.* p. 861). If the two tubes of radius r_1 and r_2 respectively are immersed to a depth t cm., and h_1 and h_2 (in centimetres of the liquid) are the pressures required to liberate bubbles, then we have

$$h_1 = \frac{a^2}{X_1} + t \quad \text{and} \quad h_2 = \frac{a^2}{X_2} + t,$$

so that

$$H = h_1 - h_2 = a^2\left(\frac{1}{X_1} - \frac{1}{X_2}\right)$$

and

$$a^2 = \frac{H}{\frac{1}{X_1} - \frac{1}{X_2}}.$$

To calculate the first values of X_1 and X_2 for the result at the lowest temperature, the means of the values of a^2 given by Smith and by Hogness have been taken as approximate values, while in calculating the results for successively increasing temperatures the final value of a^2 for the previous temperature was taken. a^2 was then calculated by the method of successive approximations *. The above method of calculation can, of course, only be used when the level of the liquid is not sensibly altered by the volume occupied by either bubble, *i. e.*, theoretically when the surface of the liquid is an infinite plane. In the present case, where the metal is contained in a crucible 3·0 cm. diameter, this condition is far from being fulfilled, and a correction has to be made for the increase in the value of t, due to removal of

* In certain cases values of X/r for $r/a=2{\cdot}0$ approximately were required. The value of X/r for $r/a=1{\cdot}8$ (which appears to be the highest value of r/a which Bashforth and Adams's tables enable us to deal with) was calculated and the curve extrapolated.

metal from the tube and the volume occupied by the bubble. In the case of the narrow tube this was neglected, and in the case of the wide tube the method of correction can be illustrated by taking the case of tin at 253°. Taking $\gamma = 500$ dynes/cm., $a^2 = 0{\cdot}1460$ sq. cm., $a = 0{\cdot}3821$ cm., $\frac{r_2}{a} = 1{\cdot}466$ (r_2 is the radius of the wide tube and $= 0{\cdot}56$ cm.), $h = 15{\cdot}5$ cm. of water, and D^{250} for tin $= 6{\cdot}982$. From Sugden's table we find X_2 to be equal to 0·2334, hence $h = \frac{a^2}{X_2} + t$, where h is 2·220 cm. of Sn, we find $t = 1{\cdot}595$ cm. of Sn. We have then to determine the capillary depression in the wide tube.

Now

$$2\gamma = rd\,hg \quad (r = 0{\cdot}46 \text{ cm.})$$

(for this correction term the angle of contact is taken as 180°), hence the height of metal in the tube is 1·278 cm. The volume of metal displaced will be

$$3{\cdot}142 \times (0{\cdot}46)^2 \times 1{\cdot}278 + \frac{\frac{4}{3} \times 3{\cdot}142 \times (0{\cdot}56)^3}{2} \text{ c.c.}$$

if the volume of the bubble is taken approximately as a hemisphere. This amounts to 1·218 c.c. The volume between the wide tube and the wall of the crucible amounted to 6·084 c.c. per centimetre height, so that the increase in t * amounts to 0·200 cm. As this increased height operates when a bubble is blown from the wide tube but not from the narrow one, it must be added to H.

The results, which are the means of a large number of determinations, are given in Table I. The pressures P are given in centimetres of water, and the densities have been taken from a paper by Day and Sosman †. The tin used contained at least 99·99 per cent. of that metal, and the lead contained only 0·002 per cent. of Cu and 0·002 per cent. of Fe.

* This is not quite exact. The value of t calculated in this manner is the depth of liquid after the metal has been displaced, and the capillary depression should strictly be subtracted from the original rather than from the final level. The error introduced in this way acts in the opposite direction to the error involved in taking the angle of contact as 180° in calculating the depression.

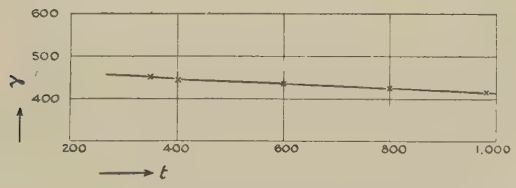
† Amer. Journ. Science, 1914, xxxvii. p. 10.

TABLE I.

Temp. °	P. Wide.	P. Narrow.	a^2 (cm.)^2.	γ dynes/cm.
	Mercury.			
19	14·4	26·7	·0708	470
	Tin.			
253	15·5	31·0	0·1538	526
299	15·5	31·05	0·1547	527
401	15·55	31·05	0·1558	526
600	15·6	31·10	0·1584	525
800	15·6	30·95	0·1596	520
964	15·6	30·80	0·1601	514
	Lead.			
350	19·9	31·5	0·0865	453
402	20·0	31·4	0·0857	446
600	20·35	31·4	0·0858	436
800	20·5	31·2	0·0855	425
982	20·6	30·9	0·0850	414

The results for lead are shown graphically in fig. 2, and it will be seen that the relation is practically linear. Extrapolation to the melting-point (327°) gives for γ, 452 dynes/cm.

Fig. 2.



This agrees very well with Hogness, who found 444 dynes/cm. Hogness gives the empirical formula

$$\gamma = 444 - 0{\cdot}077\,(t - 327)$$

connecting γ and temperature, which gives a decrease of approximately 10·0 per cent. in the value at 980°. The value found in the present work gives a decrease of approximately 8·0 per cent. Hogness's value for tin at the melting-point, 531, also agrees very well with the present value 526. If the decrease in surface tension at 980° is calculated from his formula $\gamma = 531 - 0{\cdot}080\,(t - 232)$, a value of 12·0 per cent.

approximately is obtained. This is not in agreement with the present work, where a decrease of only 2·5 per cent. has been measured. The above equation was derived from measurements at only three points, 262°, 319°, and 396°, and the last value (396°) was actually higher than the second one.

As pointed out by Hogness, the values for mercury given in the literature vary between 340 and 575 dynes/cm. The figure obtained with the present apparatus for mercury at 19°, 470 dynes/cm., differs only by 1 per cent. from that obtained by Hogness at 20°, 465 dynes/cm.

The values obtained by different observers for tin and lead are given in the following table :—

Observer.	Temp. °	Tin.	Temp. °	Lead.
Quincke *	232	681	327	537 dyncs/cm.
Siedentopf *	232	612	327	509 ,,
Grunmach *	232	352	327	482 ,,
Smith	(750–910)	480	(770–780)	424·5 ,,
Hogness	232	531	327	444 ,,
Author	232	526	327	452 ,,

* These values have been taken from the table given by Hogness.

McLeod † has suggested the relation

$$\gamma = C\,(D-d)^4,$$

where D is the density of the liquid, d that of the vapour, and C is a constant. Ferguson ‡ has put forward

$$\gamma = \gamma_0\,(1-bt)^n,$$

and states that for non-associated liquids $n = 1{\cdot}21$ gives very good results. In a later paper § he has shown that by eliminating $(1-m)$ between this equation and Katayma's form of the Ramsay Shields equation, viz.:

$$\gamma\left(\frac{M}{D-d}\right)^{2/3} = A\theta\,(1-m),$$

McLeod's relation is obtained if $n = 1{\cdot}20$. Sugden ‖ has shown the constancy of $\frac{\gamma^{1/4}}{D}$ for a large number of non-associated liquids up to temperatures approaching the critical

† Trans. Faraday Soc. xix. p. 38 (1923).
‡ Phil. Mag. (6) xxxi. p. 37 (1916).
§ Trans. Faraday Soc. xix. p. 407 (1924).
‖ Trans. Chem. Soc. cxxv. p. 32 (1924); *ibid.* cxxv. p. 1167 (1924).

temperature, but found that the value of this constant increased slowly with rise of temperature for liquids which are considered to be associated, *e. g.* methyl and ethyl alcohol, acetic acid, amines, etc. The rise in this constant for non-associated liquids up to the boiling-point was usually of the order of 0·5 per cent., while for ethyl alcohol the change was approximately 2·0 per cent. from 20° to

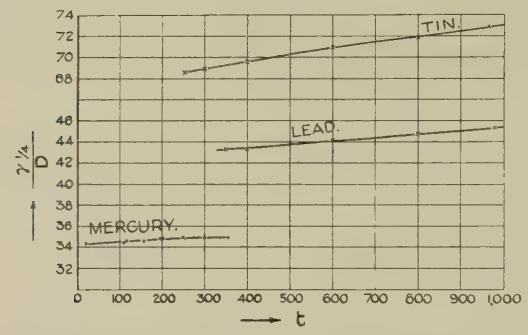
Table II.

Temp. °	γ.	D.	$\frac{\gamma^{1/4}}{D}$.
Mercury.			
20	465	13·54	·343
22	461	13·54	·342
110	447	13·33	·345
112	454	13·33	·346
155	441	13·22	·346
195	434	13·13	·348
200	436	13·12	·348
251	421	12·99	·349
300	405	12·87	·349
303	408	12·87	·349
354	394	12·76	·349
Tin.			
253	526	6·982	·686
299	527	6·943	·690
401	526	6·875	·696
600	525	6·755	·709
800	520	6·637	·719
964	514	6·542	·728
Lead.			
350	453	10·658	·433
400	446	10·597	·4335
600	436	10·359	·441
800	425	10·132	·448
982	414	9·935	·454

the boiling-point, and 5·0 per cent. to 230°. In Table II. the values of $\frac{\gamma^{1/4}}{D}$ are given for mercury (calculated from

Hogness's results) and for tin and lead (d has been neglected). They are also shown graphically in fig. 3. It will be seen

Fig. 3.



that the value of this function increases about 2·0 per cent. for mercury and about 5 per cent. for tin and lead. The increase in the value for mercury takes place be ween 20° and 200°, after which the graph is a straight line. When we consider that a change in this "constant" is found comparable with that obtained for associated liquids over a much greater range of "reduced" temperature, then if the constancy of McLeod's relation is accepted as a criterion of an unassociated liquid, both tin and lead in the liquid state appear to be highly associated.

It is proposed to determine the surface tension of a number of other metals and alloys by this method.

Summary.

The surface tensions of liquid tin and liquid lead have been determined between the melting-points and 1000° (approximately).

The values obtained at the lower temperatures agree very well with Hogness's results, but the temperature coefficient of surface tension for tin obtained by him has not been confirmed.

Evidence is brought forward to show that both these metals in the liquid state may be highly associated.

The author would like to thank Dr. W. Rosenhain, F.R.S., for his interest and advice during the progress of this work, and Mr. J. Trotter for assistance in the experimental portion.

XXIX. *Determination of the Modulus of Elasticity by Dynamical Methods.* *By* H. W. Swift, *M.A., B.Sc.**

The True Modulus of Elasticity.

It is well known that the strain or deformation of a material is not in general uniquely determined by the existing system of applied stresses. The elongation of a specimen in simple tension, for example, depends in many cases not only upon the load itself but also upon the method by which this load has been applied, the period over which it has been applied, and the previous elastic history of the specimen.

The deformation which follows a change of static loading may, in the most general case, it appears, be resolved into three separate constituents :—

a. The strain which develops simultaneously with the change in stress, and of which it may be regarded either as the cause or effect. This strain is essentially reversible in nature.

b. A deformation essentially permanent and irreversible which develops more slowly and with the passage of time approaches (in an irregular but roughly logarithmic way) its final value.

c. A strain which develops slowly in a similar way to the permanent set, but which is reversible. This strain is made evident in the partial recovery ("elastic after-strain") which follows the removal of load from so-called semi-elastic materials or from materials which have been overstrained, and in the reversible creep which occurs with elastic materials at high temperatures even under stresses which have apparently no permanent residual effect.

The processes which give rise to these changes are not known, but from the simple fact that strain may have this composite nature it follows that, unless some regard is paid to the factor of time in its definition, the Modulus of Elasticity has no real physical significance and a restricted practical value. Hopkinson † has suggested, with reference to metals at high temperatures, that it would be reasonable to define Young's Modulus under such conditions as the ratio of the stress to the instantaneous strain, and this might well be accepted as the general definition of a quantity

* Communicated by the Author.

† Proc. Roy. Soc. lxxvi. A, p. 424.

which would have a clear significance, eliminate (in theory at any rate) the effects of both types of "creep," and simplify the conception of elasticity in overstrained materials.

In the case of the elastic materials in common use, below the elastic limit there will as a rule be no creep, so that the effect of time is negligible and values of the modulus obtained at all rates of loading will be practically identical with the true adiabatic elastic modulus. With materials in a plastic or imperfectly elastic state the rate of loading has a considerable effect upon the form of the stress-strain curve, and the strain due to creep is as a rule large compared with the elastic strain. It follows that any tendency to creep is likely, at any normal rate of loading, to have a large effect upon the value of the apparent modulus. Under such conditions values for the "modulus" have no significance unless methods are employed which eliminate the effects of creep entirely. The removal and re-application of a load above the elastic limit give rise to quasi-elastic strains, but it is not possible to say with confidence which portion, if any, of the stress-strain curves so produced corresponds to a truly elastic change, unless the material becomes hardened by prolonged overstrain, in which case there is no assurance that the modulus itself has not undergone modification.

It would appear that where the two types of strain are co-existent no statical method, however rapid the loading, can be relied on to give satisfactory results. There are methods, however, which are able to effect a separation of the two types, and these depend upon the oscillatory movements which take place about the position of equilibrium under small disturbances. The period of such free vibrations is dependent upon the elastic constituent of the strain entirely. The plastic deformation only affects them in so far as it tends to damp them out. It follows that where the period of oscillation can in some simple manner be correlated with the elastic modulus, it affords a very satisfactory method for the determination of this quantity under any condition of stress and strain, and the value so obtained will measure the instantaneous resistance of the material to deformation, and will therefore represent the true elastic modulus.

Dynamical methods of this kind are frequently used to determine the modulus of rigidity, and also to find Young's Modulus for the material of helical springs. To determine the elastic modulus for a straight rod of any section there are two modes of vibration available—longitudinal and transverse.

With most engineering materials the observation of longitudinal vibrations is not easy, the amplitude under ordinary conditions being very small and the periodicity very great. An exception to this is found in the case of wires, where, by the artifice of fixing the wire in span and loading it transversely, the apparent amplitude of vibration can be increased and the periodicity reduced. In this way wires of gauges in common use can, on a convenient scale, be caused to produce elastic oscillations which can be easily observed and timed. Calculation of the modulus is not a difficult matter and the method is found in practice to give very consistent results, even while plastic strain is visibly going on. It has a great additional advantage in that any desired value for the mean tension in the wire may be obtained by adjustment of the load and sag, and the elastic constant so obtained refers to the material in this particular condition.

With sections of greater stiffness this method becomes impracticable, and flexural vibrations are more suited to observation. For practical purposes the most convenient modes of flexural vibration are :

a. Vibrations as a cantilever.
b. Vibrations as a simply supported beam.

It is not possible by these means, nor apparently by other similar methods, to obtain values of the modulus at high stresses, since the period of lateral vibrations becomes less and less dependent upon the elastic properties of the rod as its tension increases. In the outcome this limitation does not appear to be serious, for, with metals at least, it is found from experiments with wire that the true elastic modulus is to all intents and purposes independent of stress or condition of the material over the whole range up to fracture. Hence it would appear that the results obtained by the method of flexural vibrations, at necessarily low stresses, afford elastic data applicable under any conditions. We shall give this method first consideration.

Flexural Vibration of Rods.

Theoretical Basis of the Method.

The conditions which determine the free oscillation of a flexible rod are of course identical with those controlling the rapid vibrations which are commonly associated with the

problems of whirling in shafts, and in most cases the same equation of motion can be applied without error. Thus, provided only that external forces, such as gravity, have an effect which is either negligible or constant during oscillation, the fundamental equation is:

$$EI\frac{\partial^4 y}{\partial x^4}+\frac{w}{g}\cdot\frac{\partial^2 y}{\partial t^2}=0,$$

where w is the weight per unit length of rod.

For a rod of uniform section the general solution of this equation is:

$$y=\cos(pt+\alpha)\,.\,[A\cos mx+B\sin mx + C\cosh mx+D\sinh mx],$$

in which expression the constants are determined by the length of the rod and conditions of support, and m is related to the period t of a complete vibration:

$$m^4=\frac{4\pi^2}{t^2}\cdot\frac{w}{gEI}.$$

It follows that if we are able in any instance to evaluate m, and to determine the period t by experiment, then the modulus of elasticity for the material of the rod may be deduced from the relation:

$$E=\frac{1}{m^4}\cdot\frac{4\pi^2}{t^2}\cdot\frac{w}{gI},$$

or its "stiffness" from the relation:

$$EI=\frac{1}{m^4}\cdot\frac{4\pi^2}{t^2}\cdot\frac{w}{g}.$$

It remains to evaluate m for the conditions of support which are likely to be useful in practice.

a. *Rod Simply Supported.*

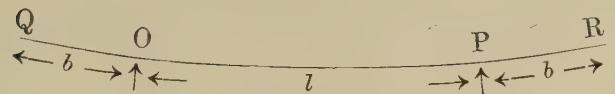
For a rod of any uniform section, oscillating in a principal plane of inertia and simply supported at the ends, the value of m is well known.

For the fundamental vibration $m=\frac{\pi}{l}$.

For a rod under similar conditions, but supported symmetrically at a distance from either end—as may be necessitated in practice by questions of convenience or

stiffness—the value of m may be found as follows :

Fig. 1.



Taking origin at O and measuring x in the direction OP, the equations giving the displacement of any point from its position of statical equilibrium are :

$$\text{for OP, } \frac{y_1}{\cos(pt+\alpha)} = A_1 \cos mx + B_1 \sin mx + C_1 \cosh mx + D_1 \sinh mx$$

$$\text{for OQ, } \frac{y_2}{\cos(pt+\alpha)} = A_2 \cos mx + B_2 \sin mx + C_2 \cosh mx + D_2 \sinh mx.$$

The end conditions are :

$$x=0,\ y_1=0, \quad y_2=0, \qquad x=0,\ \frac{\partial y_1}{\partial x} = \frac{\partial y_2}{\partial x},$$

$$x=l,\ y_1=0, \quad x=-b,\ \frac{\partial^2 y_2}{\partial x^2} = \frac{\partial^3 y_2}{\partial x^3} = 0, \qquad \frac{\partial^2 y_1}{\partial x^2} = \frac{\partial^2 y_2}{\partial x^2},$$

$$x=\frac{l}{2},\ \frac{\partial y_1}{\partial x} = 0.$$

From these eight conditions it is possible to eliminate the seven ratios between the constants $A_1A_2B_1B_2C_1C_2D_1D_2$ and to deduce the relation :

$$\tanh\frac{ml}{2} + \tan\frac{ml}{2} = 2 \cdot \frac{1+\sec mb \operatorname{sech} mb}{\tan mb - \tanh mb},$$

which determines the value of m.

In order to obtain this expression in a form suitable for practical application, let the right-hand side be expanded in terms of mb. The result up to and including terms of the sixth order in $\frac{1}{mb}$ is

$$\tanh\frac{ml}{2} + \tan\frac{ml}{2} = \frac{6}{m^3b^3},$$

and it can be shown that for small values of the ratio $\frac{b}{l}$ a close approximation to the exact solution is given by

$$\frac{ml}{2} = \frac{\pi}{2} - \frac{m^3b^3}{6}.$$

Hence $$\frac{ml}{2}=\frac{\pi}{2}\left\{1-\frac{\pi^2b^3}{3l^3}\right\} \text{ nearly,}$$

and the value of the modulus for short overhangs is

$$E=\frac{4}{\pi^2}\cdot\frac{wl}{gIt^2}(l^3+\tfrac{40}{3}b^3).$$

Experimental tests show that this relation holds well for values of the ratio $\frac{b}{l}$ up to 0·2, the correction in that case being over 10 per cent.

For values of the overhang not exceeding $\frac{1}{12}$ span the correction is less than 1 per cent. and may usually be neglected.

b. *Rod as Cantilever.*

For a fairly stiff rod of uniform section fixed as a horizontal cantilever the value of m is well known:

$$m=\frac{1\cdot875}{l}.$$

When the length l is measured along the rod, this value is found to give good results when the deflexion at the end does not exceed about $l/6$. For more flexible sections the rod is more conveniently fixed as a vertical cantilever, but the value of m will in that case be influenced by the fact that gravity will increase (if the rod hangs downwards) or decrease (if it stands erect) the elastic restoring force, and will therefore have an effect upon the periodicity.

The equation of motion in this case contains an additional term due to the effect of gravity, and for a rod hanging vertically downwards takes the form:

$$EI\frac{\partial^4y}{\partial x^4}+w\frac{\partial y}{\partial x}+\frac{w}{g}\frac{\partial^2y}{\partial t^2}=0,$$

where w is the weight per unit length of rod.

If we assume as a solution:

$$y=u\sin(pt+\alpha),$$

where $\begin{cases}u \text{ is a function of } x \text{ independent of } t,\\ p,\ \alpha \text{ are independent of } x,\end{cases}$

then u must satisfy the equation:

$$\frac{\partial^4u}{\partial x^4}+\frac{w}{EI}\frac{\partial u}{\partial x}-\frac{p^2w}{gEI}u=0.$$

If the effect of gravity is negligible the centre term disappears. In a large range of useful cases its value will be small. Under these circumstances it is justifiable to apply an approximate method for the solution of the equation :

$$D^4 + \frac{w}{EI} D - \frac{p^2 w}{gEI} = 0,$$

or $$D^4 + \alpha D - \beta^4 = 0, \text{ say.}$$

Writing $D = \beta + \epsilon$ where ϵ is small, we find

$$\epsilon = -\frac{\alpha}{4\beta^2} \text{ nearly.}$$

Hence $$D = \beta - \frac{\alpha}{4\beta^2},$$

and the complete approximate solution may be written :

$$u = (A \sin \beta x + B \cos \beta x)(1 + \gamma x) + (C \sinh \beta x + D \cosh \beta x)(1 - \gamma x),$$

where $$\gamma = \frac{1}{4p} \sqrt{\frac{wg}{EI}}.$$

The end conditions are :

$$x = 0, \quad u = 0, \quad \frac{\partial u}{\partial x} = 0,$$

$$x = l, \quad \frac{\partial^2 u}{\partial x^2} = 0, \quad \frac{\partial^3 u}{\partial x^2} = 0.$$

By applying these conditions and eliminating ABCD, an equation results which may be reduced to the form :

$$1 + \cos \beta l \cosh \beta l = \frac{2\gamma}{\beta} (\cos \beta l \sinh \beta l - \sin \beta l \cosh \beta l),$$

where $\frac{\gamma}{\beta}$ is small.

The approximate solution of this equation is

$$\beta l = \beta_0 l + \frac{2\gamma}{\beta},$$

where $\beta_0 l$ is the value (1·875) of βl when $\gamma = 0$.

Hence the angular velocity p corresponding to the vibratory motion is given by

$$\left[\frac{p^2 w}{gEI}\right]^{\frac{1}{4}} l = \beta_0 l + \left[\frac{g^3 w}{p^6 EI}\right]^{\frac{1}{4}},$$

and knowing the period $t=\frac{2\pi}{p}$ the modulus of elasticity can be found by the formula :

$$E=\frac{4\pi^2 l^4 w}{\beta_0^4 g I t^2}\left(1-\frac{2gt^2}{4\pi^2 l}\right)$$

$$=3{\cdot}20\frac{wl^4}{gIt^2}\left(1-{\cdot}051\frac{gt^2}{l}\right) \text{ nearly.}$$

If the rod be fixed as a cantilever standing erect, the signs of α, γ in the above analysis will be reversed, and we have finally :

$$E=3{\cdot}20\frac{wl^4}{gIt^2}\left(1+{\cdot}051\frac{gt^2}{l}\right) \text{ nearly.}$$

c. *Rod Simply Supported and Loaded at Centre.*

The vibration of a uniform rod with a single concentrated load is treated exactly by Dunkerley *, who obtains an implicit equation in m. If the concentrated load is central it is possible to reduce this equation to the form :

$$\frac{\left\{1-\frac{\alpha}{4}(\tan\theta-\tanh\theta)\right\}\left\{1+\frac{\beta}{4}\frac{\tan\theta-\tanh\theta}{\tan\theta\tanh\theta}\right\}}{\tan\theta-\tanh\theta}=0,$$

where $\alpha=\frac{Ww^2}{m^3 gEI}$, $\beta=\frac{w^2 I'}{mEI}$, $\theta=\frac{ml}{2}$.

The solution to the present problem is

$$\tan\theta-\tanh\theta=\frac{4}{\alpha}=\frac{4w}{Wm},$$

and the value θ of $\frac{ml}{2}$ for any value of the ratio $\frac{W}{wl}$ is given by the equation :

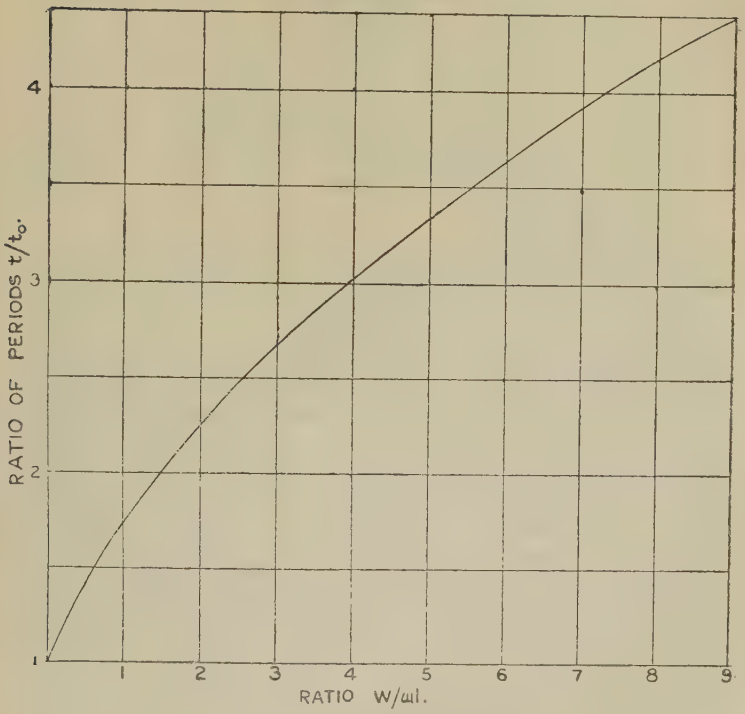
$$\theta(\tan\theta-\tanh\theta)=\frac{2wl}{W}. \quad . \quad . \quad . \quad . \quad \text{(i.)}$$

For assumed values of θ a curve can be plotted (fig. 2) and the relation between $\frac{wl}{W}$ and $m=\frac{2\theta}{l}$ can be established to any required degree of accuracy.

It is of interest to note that $\theta=\frac{\pi}{4}$ when $\frac{W}{wl}$ is approximately 7, showing that by loading a rod centrally to this extent the period of vibration will be quadrupled.

* Dunkerley, Phil. Trans. Roy. Soc. vol. clxxxv.

Fig. 2.—Effect of Central Loading on Periodicity of simply supported Beam.



Technique of the Method.

(a) *Accuracy.*

The form of the expressions obtained for the modulus makes it clear that some of the measurements require more careful determination than do others. For example, in each case the modulus varies inversely with the square of the period of oscillation, so that errors in timing will be doubled. Where no artificial device is available for the counting of vibrations, accurate results cannot ordinarily be expected if the period is much less than 0·3 second. This limits to some extent the convenient application of the method and is discussed in more detail later. From the present experimental work it appears that with this reservation a reliable value for the periodicity can be expected if two tests are made, each over not less than a hundred oscillations and of not less than one minute's duration.

In determinations by the lateral vibrations of rods errors in the applied value of $ml=\theta$ will be quadrupled, and it follows that this must be known with more than usual accuracy. Approximate relations which are admirably suited to the estimation of whirling speeds require examination before they can be accepted for the determination of the modulus of elasticity, and for that reason approximate methods have where possible been avoided in the theoretical treatment and where unavoidable have been checked experimentally.

Careful measurement of the cross-section and length of the bar will also be necessary. For similar accuracy greater care is required in the computation of the sectional moment of inertia than merely of the sectional area. If the stiffness EI is required, of course, no measurement of the cross-section is necessary. There is no difficulty in measuring the length with sufficient accuracy when the rod is simply supported, but in other cases it is important that the end which is encastré should be very securely fastened in a massive clamp. Otherwise insensible movement in the clamp may increase the effective length of the rod and seriously prejudice the results. In the present experiments the bars used were clamped horizontally in a 25 ton testing machine over 18 inches of their length, and in the case of a round bar one inch in diameter it was found that a measurable error was introduced if the distributed pressure fell to 5 tons.

(b) *Experimental Results.*

Experiments were made in the first place to test the accuracy of the methods proposed and to verify the results obtained.

a. In Table I. are shown values of the modulus obtained by the method of flexural vibrations compared with determinations made by extensometer on a short length of the same rod, and also by measurement of the deflexion of the rod as a simply supported beam with central load. The agreement in most cases is considered good. The heavier bars show a tendency to give low results when fixed as vertical cantilevers, but this is almost certainly due to imperfect rigidity in the clamps employed, the importance of which has been mentioned. No present explanation is offered for the low figure obtained from bending of the flat section. The tests, however, seem to afford satisfactory evidence that the method is practicable and capable of good accuracy, and indicate that it may generally be applied with

less trouble and more confidence to stiff rods when simply supported. With lighter and more flexible rods, however,

TABLE I.

Comparative Values of Young's Modulus obtained by Statical and Dynamical Methods.

Rod.	Values of Young's Modulus.				
	Extensometer.	Oscillations.			Bending.
		↑ ↑	=	Vertical.	
STEEL:					
$\frac{3}{4}$ in. round.....	29·7	30·2	29·9	29·8	29·9
1 in. round.....	29·5	29·7	29·4	(28·6)	29·6
1 in. × $\frac{1}{2}$ in. flat.	28·9	29·0	28·5	28·5	(27·8)
$\frac{3}{16}$ in. round ...	29·5	—	29·4	—	29·0
COPPER:					
$\frac{5}{8}$ in. round	17·9	18·2	18·0	17·9	17·9
Same Annealed...	17·5 18·3	18·1	17·9	17·6	—

it is found that oscillations are more readily made to persist under encastré conditions, and in these cases secure clamping presents no difficulty.

b. Table II. gives the results of the tests made to verify the correction proposed for the overhang of simply supported rods. It will be seen that the results are reasonably consistent, and there is no serious deviation up to an overhang at each end of a fifth of the span.

TABLE II.

Test of Correction for Overhang.

$\frac{3}{4}$ in. round, Steel.		
Ratio of Overhang. b/l.	Young's Modulus. E.	Correction Applied. per cent.
·005	30·3	nil
·065	30·2	0·4
·10	30·1	1·3
·14	30·1	3·7
·18	30·0	7·7
·21	29·8	12·5

c. Experiments were made to confirm the relation between $ml=\theta$ and $\frac{wl}{W}$. In these tests a steel rod and also a copper tube were used, and out of 25 determinations of θ none differed by more than $\frac{1}{2}$ per cent. from the theoretical value derived from equation (i.). The greatest load was sixteen times the weight of the rod.

d. Table III. gives values of the product EI for sections of a form inconvenient for extensometer tests. These are derived from oscillations and from careful measurements of static deflexion under load. The bar was in each case simply supported (on light rollers) and in some cases was subjected to a central load.

TABLE III.

Determination of Stiffness EI by Oscillations.

Section.	Value of EI.	
	Bending.	Vibration.
Steel: 1 in. angle...	419×10^3	421×10^3
$2\frac{1}{2}$ in. angle..	$10{\cdot}5\times10^6$	$10{\cdot}6\times10^6$
Copper: $\frac{5}{8}$ in. tube..	315×10^2	310×10^2

e. As a test of the validity of the method in the case of imperfectly elastic materials, the copper rod already used was annealed along its entire length and then subjected to tests by vibrations and by extensometer. The bending test was impracticable as the bar sagged continually under its own weight. In spite of this oscillations persisted sufficiently to give the results shown in Table I. These seem to afford definite proof that the method does effectively separate the elastic extension from plastic creep and also suggest that the true elastic modulus is not appreciably modified by annealing. The slight difference recorded may be due to incorrect measurement of the section, which showed slight irregularities owing to scaling during the process of annealing. The stress-strain relation revealed by the extensometer was nowhere linear, and the figures given in the table are derived from the earlier part of tests during which the load was being removed from the specimen after several applications.

(c) *Applications.*

The method of flexural vibrations is put forward primarily for its scientific value as one capable of separating the truly elastic from other forms of strain and of determining the true elastic modulus. For this purpose it appears to be admirably suited. The apparatus required is of the simplest type, no manipulative skill is necessary, and the results are reliable and accurate.

It is not suggested that the method is able in any general way to take the place of the usual extensometer test where information is sought regarding the static stress-strain relations of a material. Any dynamical method is by nature unsuited for such a purpose. But there are certain practical cases of materials which are perfectly elastic, or materials which by mechanical treatment will become perfectly elastic before employment, in dealing with which the method of oscillations has distinct possibilities. In the first place a whole rod or bar of the material may be used for the test, so that no cutting or preparation of a specimen is necessary whatever shape the section may be, a considerable saving in the case of sections whose shape renders them inconvenient to test by extensometer. Furthermore, where a section is to be employed as a beam or strut, the quantity upon which the design is based is the product EI of the elastic modulus and sectional moment of inertia. It is this product which also determines the period of flexural vibrations, so that without any measurement of the cross-section it is possible to calculate the stiffness of the rod from a knowledge simply of its length, period of oscillation, and conditions of support. With the lighter forms of rolled and extruded sections, the sectional moment of inertia requires very careful measurement, and in such cases the method may actually give more ready and reliable information of the behaviour of the section as a beam or strut than separate determination of the moment of inertia and modulus of elasticity, which the use of an extensometer would necessitate.

The range of sections over which the method may conveniently be employed is limited by the accuracy with which the timing can be carried out. It has been pointed out that the shortest period which is likely to afford reliable results is about 0·3 second. Table IV. has been drawn up on this basis and shows the least length of a number of sections upon which tests of this kind may be satisfactorily made when the section is unloaded and simply supported at the ends. Where bars of the necessary length are available,

experiment has shown that this method of support is as a rule the most suitable. When very light rods (the 3/16 diameter tie rod referred to in Table I. is a case in point) are tested in this way, it may be found that owing to flexibility the oscillations damp out rapidly. In such cases it will be more convenient to fix the rod as a cantilever, a process which will be found to give persistency to the vibrations and will also increase their period. A similar effect to a lesser degree is obtained if the rod is made to overhang at each end of the simply supported span.

TABLE IV.

Young's Modulus by Oscillations, Unloaded in Span. Minimum Lengths Suitable.

Section (Steel).		Minimum length.
Joists:		feet
BSB 1	$3\times1\frac{1}{2}$	15
2	3×3	22
8	6×3	20
12	8×4	23
17	10×5	27
Channels:		
BSC 1	$3\times1\frac{1}{2}$	17
7	6×3	24
20	$10\times3\frac{1}{2}$	26
Angles:		
BSEA 5	$2\times2\times\frac{3}{16}$	16
9	$3\times3\times\frac{3}{8}$	20
14	$6\times6\times\frac{5}{8}$	28
Tees:		
BST 6	$2\times2\times\frac{5}{16}$	17
15	$4\times4\times\frac{5}{8}$	23

When bars are employed whose section is too stiff or whose length is too short for this method, the period of vibration may be increased by the addition of dead weights at the centre. The extent to which this device will affect the period is indicated by fig. 2, which is derived from equation (i.).

The $2\frac{1}{2}$-inch angle referred to in Table III. would have given a period of 0·123 second unloaded. By applying a central load of 306 pounds the period was increased to 0·36 second, which is readily measurable. The extent to which this artifice can be applied is determined by the beam strength of the bar. It will be noted in this connexion, that since the period is for large central loads nearly proportional

to $W\frac{1}{2}l^{\frac{3}{2}}$, whereas the maximum stress in the beam is proportional to Wl, the period for a given maximum stress will vary directly with the length l. Hence the greater the length of the bar available, the more probable is it that the vibrations can be made sufficiently slow for measurement without overstressing the material.

Oscillations of a Wire in Span with Central Load.

Consider a flexible wire of weight wl supported across a span 2M loaded centrally as shown in the figure.

Fig. 3.

The oscillations under consideration are those which would follow the sudden release of a small additional load at the centre.

At any instant we shall suppose the tension at the ends of the wire to be T, acting at an angle of θ with the horizontal, and that the central sag is Z.

Writing
$$\begin{cases} Z_0 = M \tan\theta, \\ m = \text{chord AZ}, \end{cases}$$

we have
$$\begin{cases} \delta\theta = \dfrac{\cos^2\theta}{M}\delta Z_0, \\ \dfrac{\delta T}{aE} = \dfrac{\delta m}{m} = \tan\theta \,.\, \delta\theta, \end{cases}$$

where E is the *apparent* modulus of the wire in span.

The upward force P tending in any position to restore equilibrium is

$$P = 2T\sin\theta - (W + wl).$$

Hence
$$\delta P = 2\sin\theta\,\delta T + 2T\cos\theta\,\delta\theta,$$
$$= \frac{2EaZ_0^2\cos^3\theta}{M^3}\delta Z_0 + \frac{2T\cos^3\theta}{M}\delta Z_0.$$

This will give rise to simple harmonic oscillations of period t given by

$$\frac{2Ea}{M^3}Z_0^2\cos^3\theta + \frac{2T}{M}\cos^3\theta = \left(W + \frac{wl}{2}\right)\frac{4\pi^2}{t^2 g},$$

where
$$T = \frac{W + wl}{2\sin\theta}.$$

The apparent modulus may therefore be derived from experimental figures by the relation :

$$aE = \frac{W + \frac{wl}{2}}{t^2 Z_0^2 \cos^3\theta} \cdot \frac{2\pi^2 M^3}{g} - \frac{M^3(W + wl)}{2Z_0^3 \cos\theta},$$

and since

$$\frac{Z_0}{Z} = \frac{M}{m} \cdot \frac{W + wl}{W + \frac{wl}{2}},$$

it follows that

$$aE = \frac{2\pi^2 M^3}{g} \cdot \frac{W + \frac{wl}{2}}{t^2 Z^2} \left(1 - \frac{gt^2 \cos\theta}{4\pi^2 Z}\right)\left[\frac{W}{W + wl} \cdot \sec^5\theta\right],$$

where $\sec^5\theta = 1 + \frac{5}{2} \cdot \frac{Z^2}{M^2}$ under normal conditions.

In this expression the terms in the square bracket may be regarded as corrective upon the remainder, and in a particular determination either or both may be negligible according to the conditions. It is possible where great accuracy is required that certain other corrections must be applied for curvature in span and for stiffness in the wire, but under practical conditions it will usually be found that the tension necessary to eliminate kinks and coiling in the wire will be sufficient also to render these corrections unnecessary.

It can be shown that the fractional correction for curvature in span is

$$+ \frac{w^2 m^2 aE}{12T^3}.$$

For a steel wire 0·1 inch in diameter across a total span of 50 feet, this correction is about 1 per cent. under a tension of 80 pounds.

The correction for stiffness will depend upon the means of support at the ends.

If a wire is held in flexible clips the fractional correction is $-2\sqrt{\frac{EI}{Tm^2}}$, and for the same steel wire is below 1 per cent. for tensions above 60 pounds. In the case of a wire clamped horizontally at the ends this correction is doubled.

Experimental Verification.

a. In order to check the truth of these results and the accuracy of the method, experiments were made with steel piano wires whose elastic range was known to be large.

The wire under test was fixed across a span of about 35 feet, each end being held in a light clamp carried on a small radial ball-bearing to ensure flexibility. The spindles carrying the bearings were bolted firmly to the under side of a stiff girder. The central dip of the wire under test was measured on a steel scale which was suspended from the girder close to the wire and calibrated by means of a dumpy level. The tension in the wire was controlled by variations in the sag and load.

Determinations were made covering a range of tensile stress up to 80 tons per square inch with various values of the dip, and the results showed that provided the tension was above a certain minimum (about 40 pounds) the value of the modulus deduced was consistent and agreed well with the values obtained by statical methods. Over a hundred determinations were made, and with two or three exceptions all were within 1 per cent. of the mean values.

It was concluded from these tests that the method was free from systematic errors and capable of good accuracy.

b. The ability of the method to separate elastic from other types of strain was tested and confirmed by the use of a soft copper wire.

In spite of a final elongation of about 35 per cent. and in spite of the continuance of a visible creep during many of the periods of test, the value of the modulus (calculated on the sectional area at the time of test) was found to correspond with that obtained by statical methods during unloading (after prolonged straining), and to be constant for all values of the tension up to the point of fracture. It should be pointed out that in some instances immediately following an addition of load the creep was so rapid that oscillations were damped out before a determination of periodicity could be made, but there was in no case any evidence of variation in the period.

It seemed reasonable to conclude from these experiments that the method does effectively eliminate all but elastic strains, and gives a consistent value for the true elastic modulus.

c. The method was now applied to investigate the elastic properties of certain other wires, soft iron, hard drawn brass, and duralumin being employed.

The values of the modulus obtained over the elastic range agreed well with the results of statical methods and are shown in Table V. In order to determine the effect of plastic strain and high stresses upon the elastic properties of the wires, the experiments were continued at tensions above the elastic limit. The damping effect of creep was

sometimes evident with the iron wire, and in order to reduce the sag to convenient values it was necessary to shorten the

TABLE V.

Modulus for Wires by Oscillations.

Wire.	Value of E.	
	Statical.	Oscillation.
Piano	28·5	28·7
„ (annealed)	28·4	28·8
Iron	27·3	27·4
Brass	14·9	14·9'
Duralumin	10·25	10·3
Copper (annealed)	15·7	15·85

wires after permanent set had begun to develop. Calculations were based in each case upon the sectional area at the time of test. The results showed that the value of the modulus is substantially the same at all tensions up to the point of fracture with each of the wires employed. A progressive diminution amounting finally to 3 per cent. was recorded in the case of the brass wire at high tensions, but no systematic change whatever could be detected in the soft iron or duralumin wires.

The experiments described above were carried out at the University of Leeds.

CONCLUSIONS.

The results of the experiments with copper, iron, duralumin, and brass wire give definite support to the opinion that truly elastic strain is quite independent of any other form in development as well as origin, and show that it is possible to effect with certainty a separation in stress-strain relations between the elastic and non-elastic components of strain. They suggest moreover that elasticity is a definite inherent property of materials which is not destroyed by mechanical treatment and overstrain, and that its modulus remains practically unaffected by the elastic history and condition of the specimen. It will be interesting to trace the effects on this constant of heat treatment and temperature.

XXX. *The Variation of Pressure with Temperature in Evacuated Vessels.* *By* N. R. Campbell. (Communication from the Staff of the Research Laboratories of the General Electric Co., Wembley *.)

Summary.

If a well baked and exhausted glass vessel is carried through a cycle of heating to a temperature T_a and cooling to a temperature T_b, a condition is reached rapidly in which the pressures p_a, p_b, at these temperatures are repeated. If T_a is varied while T_b is fixed, both p_a and p_b are functions of T_a which depend also in a complicated manner on the constitution and preparation of the vessel.

If to this cycle is now added a stage in which the gas is "cleaned up" by the discharge, both p_a and p_b decrease with repetition of the cycle, until final values are reached which are again both functions of T_a, but now depend much less on the constitution and preparation of the vessel. If $T_a = 120°$ C., $T_b = 20°$ C., p_b is of the order of 10^{-5} mm.

If the walls of the vessel are coated with a layer of metal (Ni, Mo, W) the statement of the first paragraph remains true; but, while the clean-up still produces a temporary reduction of pressure, it does not produce the progressive permanent change described in the second paragraph. If, in place of these metals, Mg, Zu, Cu, Ag are used, subsidiary complications enter that are discussed in the test.

Attempts to determine by various methods the nature of the residual gas involved in these changes were not very successful, but indicate (in accordance with expectation) that H_2O and CO_2 are the main constituents.

The facts relating to the metal-coated vessels seem in accordance with existing ideas, but throw no light on the still doubtful question what is the means by which the discharge promotes adsorption of gas. The more complicated facts relating to the bare glass vessels require more explanation. A very tentative theory is suggested, according to which the discharge in such vessels, besides promoting adsorption, induces a chemical reaction involving the glass which leads to the permanent removal of some of the gas; at the same time the glass is capable of disolving the gas with the formation of saturated solutions which have at the temperature T_a the vapour-pressure p_a; gas is continually introduced into the vessel from the outside by diffusion of these solutions through the glass, and prevents p_a from falling below this value in virtue of the removal of gas by the chemical reaction.

* Communicated by the Director.

Some practical conclusions arising from the facts described are mentioned. Permanent low pressures ($< 10^{-6}$ mm.) in sealed-off vessels appear to be obtainable only if the glass walls are coated with metal. A reason is given why gas adsorbed on a metal surface cannot be removed by prolonged baking of the glass vessel in which it is contained, although it can be removed with great ease and rapidity by heating the metal in the cool glass vessel.

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(1) *Outline of the Observations.*

IF a glass vessel is baked at a temperature T during exhaustion to a low pressure p, sealed off and heated to a temperature T′ less than T, the pressure will rise and approach asymptotically a pressure p' greater than p. This fact appears to have been established first by Shrader * ; some additional facts were recorded in a previous paper from these laboratories †. We now propose to describe a more detailed study of the changes of pressure associated with changes of temperature in well-baked and well-exhausted vessels.

The vessels were constructed as ionization gauges. The walls were composed of four different glasses, A, B, C, D ; the cathode was always a tungsten filament ; the grid and anode were usually of nickel, but sometimes of molybdenum or tungsten. These changes in the materials of the vessel, which were accompanied by changes of geometrical form, had no ascertainable effect on the results, and accordingly it is not necessary to describe them in detail ; but particulars of the four glasses are given in an appendix.

After the vessels had been well exhausted at a temperature not less than 380° C., they were subjected to three operations :—(*a*) heating to a temperature T_a which lay between 50° and 200° C. ; (*b*) cooling to "room temperature" T_b between 13° and 20° C. ; (*c*) "cleaning-up" or reduction of pressure to p_c by the passage of a suitable discharge from the thermionic cathode.

Since in (*a*) and (*b*) the pressure approaches a final value asymptotically, a slow change being still perceptible after 24 hours, it was necessary practically to fix conventionally the period of each of these operations. The periods ranged from 20 to 44 hours ; the effects of variation within this range were masked by other irregularities. Again no significance must be attributed to the

* J. E. Shrader, Phys. Rev. xiii. p. 434 (1919).

† Research Laboratories of the G. E. C., Phil. Mag. xlviii. p. 553 (1924).

exact values of p_c; they depend on the period and conditions of the clean-up. So long as p_c is considerably lower than the preceding p_b, its precise value is of no importance.

A typical series of observations is detailed in Table I.; the numerals in the first column serve to identify the operations and denote their order.

TABLE I.

Pressures in 10^{-6} mm. calculated from the reading of an ionization gauge, assuming that the gas is nitrogen.

	p_a.		p_b.	p_c.
	(T_a=200° C.)	(T_a=120° C.)	(T_b=13°–20° C.)	
1	—	—	13·4	—
2	—	—	—	0·6
3	—	183	—	—
4	—	—	130	—
5	—	—	—	1·3
6	—	98	—	—
7	—	—	57	—
8	—	—	—	0·8
9	—	50	—	—
10	—	—	27	—
11	—	—	—	0·1
12	—	28	—	—
13	—	—	13·6	—
14	—	—	—	0·1
15	—	35	—	—
16	—	—	13·9	—
17	—	—	—	2·1
18	—	24	—	—
19	—	—	12·8	—
20	450	—	—	—
21	—	—	290	—
22	—	—	—	1·1
23	290	—	—	—
24	—	—	140	—
25	—	—	—	0·8
26	190	—	—	—
27	—	—	100	—
28	—	—	—	1·2
29	150	—	—	—
30	—	—	80	—
31	120	—	—	1·2
32	—	—	80	—
33	—	—	—	0·8
34	130	—	—	—
35	—	—	75	—

Considering first 1 to 4, we see that the first heating produces an increase of pressure which is not reversed by cooling. (This increase would have been the same if the clean-up at 2 had been omitted.) But if, after 4, operations a and b had been repeated alternately without c, no further progressive change would have occurred; p_a and p_b would have repeated themselves, and, apart from minor irregularities (which may have been due in part to lack of control of the temperatures), the pressure would have appeared a definite function of the temperature. But when a clean-up is interpolated, as at 5, a permanent change is produced; at 6 and 7 the pressure would again be found to be a definite function of the temperature if a and b were repeated, but the values would both be lower than before the clean-up at 5. Repetition of a, b, c in cylindrical order reduces these pressures further until, from 7 to 19, the pressures at the high and the low temperatures reach final values which are unaltered even if the vessel is cleaned up.

When the temperature in a is raised, as at 20, the whole cycle of changes is repeated. There is first an increase of the equilibrium pressure at room temperature. If the vessel is heated and cooled, without intermediate clean-up, the pressure corresponding to each temperature is fixed; but the clean-up reduces these pressures gradually until a final state is reached in which the relation between pressure and temperature is unchanged by the clean-up. It is to be noted that the final pressure at T_b after heating to 200° is markedly greater than the final pressure at the same temperature after heating to 120°; the pressure is a definite function of the temperature only so long as the cycle of heating and cooling remains unchanged. In order to recover the lower value after b (*e.g.* that at 19), it would be necessary to repeat the cycle a, b, c several times, with the lower value of T_a.

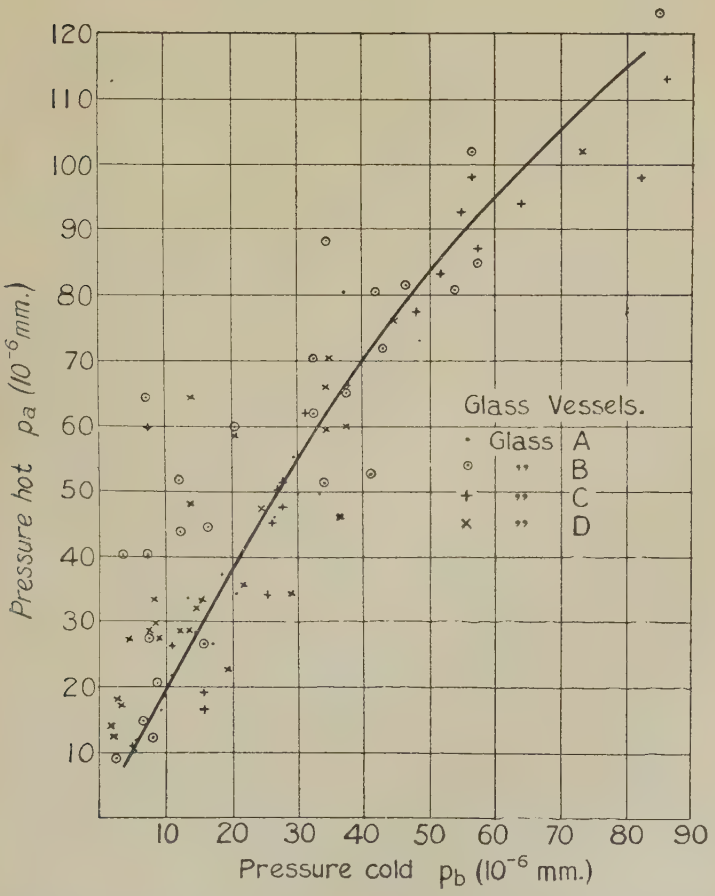
(2) *The Pressure-Temperature Coefficient. Glass Vessels.*

Observations similar to those of Table I. were made on a large number of vessels, and attempts were made to co-ordinate the absolute values of the pressures. One regularity that could be detected is shown in fig. 1. Here p_a is plotted against p_b; in each case T_a was about 120°, and p_a is compared with the p_b immediately following.

The deviations of most of the points from the line drawn through them do not exceed markedly the irregular variations shown in Table I. between the values obtained on

repetition of a cycle in which there is no progressive change. There is, however, a group of points which diverge markedly, all lying well above the line in the region of small pressures. It is probable that for these points p_b is

Fig. 1.



misleadingly small. For in all cases the reading of the ionization gauge involves a change of pressure; there is usually a slight rise of pressure, due to the heating of the electrodes, followed by a fall, due to the clean-up. The pressure recorded is always the first that can be read, and normally does not differ markedly from the maximum; but in the discrepant vessels the initial rise is abnormally large;

if the maximum had been recorded in all cases, the discrepancy would have disappeared. If it is neglected for the moment (for there are also normal points in the same region of pressure), the experiments shown in the figure indicate that there is a relation between p_a and p_b, which may be roughly described as defining a temperature-coefficient of the pressure, independent of (1) the nature of the glass and of the electrodes within the limits investigated, and (2) of whether the pressures have or have not been reduced by the clean-up. It is not certain that the relation is not also independent of T_a; for observations in which this temperature was 200° C. seem to be also near the curve; but the number of these observations was so small that it would be unwise to base much on them. Here it may be pointed out that the experiments are tedious and that each point implies a lapse of at least two days; the experiments of Table I. occupied five weeks.

Many attempts were made to discover a relation between the treatment of the vessel on the pump and the value of p_b after the first heating, but no success was obtained. Very high values of p_b can be avoided by prolonging the period of baking and pumping, but there was no evidence that the continuance of these processes for more than a few hours had any effect. A vessel which had been baked on the pump for 24 days at temperatures gradually reduced from 400° C. to 250° C. differed in no way from others sealed off after two hours' baking at 360°.

On the other hand, the important fact appeared that the final values of p_a and p_b were never very different, whatever were the initial values. The initial p_a (*i. e.* the value after the first heating to 120° C.) varied in these experiments between 40 and $1{\cdot}5\times10^{-4}$ mm.; the final value attained after many repetitions of the cycle a, b, c varied between 0·14 and $0{\cdot}06\times10^{-4}$ (in normal vessels), and there was no correlation between the initial and final values. It appears that by the repetition of that cycle vessels of this type can be reduced to a definite state which is always very nearly the same and is independent within wide limits of their previous history.

(3) *Metal-coated Vessels.*

In the exhaustion of these vessels discussed so far, the electrodes were heated in the usual way to drive off gas, but care was taken not to raise the temperature so high that there was any appreciable evaporation of the metal and

blackening of the walls. In another series of experiments the walls were deliberately blackened with evaporated nickel.

It is well known * that the pressure in a vessel can be greatly reduced by this process ; though it was originally described in connexion with the evaporation of tungsten, the reduction is not confined to this metal. Accordingly, if all gas had been carefully removed from the metal before evaporation and the vessel was sealed off immediately afterwards, the resulting pressure was very much lower than any that could be obtained by mere pumping. But if it had not been removed completely, so that the gas was evolved from the heated metal during evaporation, the pressure was not less, but usually greater, than that in the vessels with unblackened walls.

With vessels prepared in this manner, the results were definitely changed. In the first place the clean-up produced no progressive change in p_a and p_b ; the vessel could still, of course, be cleaned up by the discharge to a pressure less than p_b, but, however often the clean-up was repeated, the values of p_a, p_b obtained after the first cycle of heating and cooling remained unchanged.

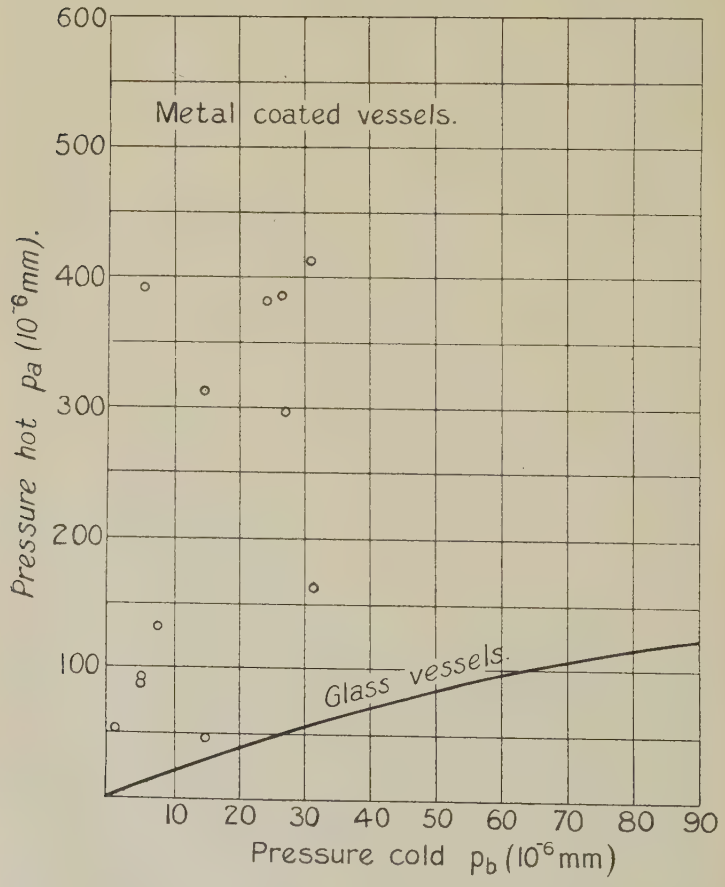
In the second place the ratio of p_a to p_b, represented in fig. 2, was considerably higher. The line in this figure refers to glass vessels and is transferred from fig. 1; the points refer to vessels of which the walls were coated with metal ; it is clear that they define a temperature-coefficient much higher than that of the unblackened vessels. The points for these vessels are necessarily fewer, because now each vessel will give only one point ; several points cannot be obtained for the same vessel by means of the clean-up. Further, the vessels shown are those in which p_a and p_b were relatively high because gas was evolved during the deposition of the metal. Those in which this evolution was avoided, and consequently the pressure was very low, cannot be shown on the same scale. The measurements at these very low pressures are somewhat inaccurate, but there was no doubt that the very highly evacuated vessels showed also the increased temperature-coefficient of the pressure. It is difficult to prepare vessels in which the pressure after sealing off and heating will have a prescribed value.

Exactly similar results were obtained when the walls were blackened with tungsten or molybdenum by exploding wires, or again when nickel was deposited from the carbonyl by warming the walls, instead of by evaporating

* *Cf.* S. Dushman, 'High Vacua,' p. 172.

the anode. In none of the matters discussed here could any difference between these three metals be detected. Attempts to use silver, copper, magnesium, or zinc failed. When silver or copper was deposited on the walls, either by evaporation or by chemical deposition, there was no equilibrium pressure at 120° or high temperatures; the

Fig. 2.



pressure increased steadily as long as the heating was continued. At the same time, the deposit changed in appearance and ultimately became transparent. It is clear that, even at this comparatively low temperature, there is some reaction between the metal and the glass which introduces a new and disturbing factor. With magnesium

or zinc again it was impossible to measure the pressure satisfactorily on the ionization gauge ; for the clean-up was so rapid that the pressure changed materially during the few seconds required to take an observation. The clean-up proceeds, though more slowly, even when no anode voltage is applied ; the mere presence of the hot filament seems to cause the disappearance of the gas in the presence of these metals, just as it does in their absence when the gas is hydrogen. But such measurements as could be made indicated again a temperature-coefficient of the metal-coated vessels greater than that for those with bare glass walls.

This difference is important in the interpretation of the results, for it leads at once to the rejection of the most obvious explanation of the progressive action of the clean-up to the glass vessels. At first this was naturally attributed to the gradual formation of a film of sputtered or evaporated metal on the walls ; for such a film will produce all the effects of a metal-coated surface even when it is invisible. But the marked difference in the temperature-coefficient of a glass vessel reduced to its final state by the clean-up and that of a vessel known to be metal coated is quite inconsistent with this explanation.

(4) *Permanence of the Clean-up.*

In this account one feature, common to the glass and the metal-coated vessels, has been left unnoticed. The low pressure produced in (*c*) by the clean-up is apparently permanent, so long as the vessel remains at room temperature ; vessels re-examined a year after they were cleaned up have shown no increase of pressure in the interval of as much as 1 per cent. On the other hand, the heating in (*a*) reverses completely the effect of the clean-up ; in the metal vessels or in the glass vessels in their final state, p_a is the same whether it is reached from p_b or from the much lower pressure p_c established at T_b by the clean-up. It may be asked, therefore, what temperature intermediate between T_a and T_b is necessary to reverse the clean-up.

There is no such definite temperature. When the cleaned-up vessel is heated, the pressure rises with the temperature more rapidly than it would if the same initial pressure had been established by mere cooling without the clean-up. If at any stage the heating is stopped and the vessel cooled, the pressure falls ; if the heating has lasted a short time, or if the increase of temperature has been so small

that p_b has never been reached, then the pressure on cooling, though higher than the initial p_c, will be less than p_b. But if it has been maintained for a sufficient length of time at any temperature at which pressure becomes greater than p_b, then the effect of the clean-up is wholly reversed and the pressure will fall on cooling to p_b, just as if the clean-up had never been performed.

If, however, the vessel is cleaned up at a temperature of 120° C., then the clean-up is not permanent; if the temperature is maintained the pressure rises slowly again to p_a. Accordingly, the permanence at room temperature is probably illusory. The truth is that the rate at which the clean-up is reversed increases rapidly with the temperature; at 20° C. it is to be measured in centuries, at 120° C. in hours. The labour of investigating the matter more nearly has therefore been judged prohibitive.

(5) *Nature of the Gas evolved.*

The experiments remaining to be recorded were directed to determine the nature of the residual gas. It was almost certainly not wholly the same in the blackened and in the unblackened vessels; for whereas in the former a thoriated tungsten filament would readily develop and maintain the high thermionic emission characteristic of thorium, in the latter the emission was never developed without "flashing" and never survived operation (*a*). But little more could be established definitely. The critical potentials of the residual gas were examined, absolute values being assigned by means of the ionization potential of Hg; only one such point could be identified certainly at the low pressures to which observations were necessarily confined; it varied irregularly between 15·8 and 17·2 volts. A comparison was made with vessels filled on the pump with H_2, CO_2, CO, H_2O. The last three gases all have critical potentials within this range, while that of hydrogen is less than 14·0 volts. The method would seem, therefore, to indicate that hydrogen is never present in considerable quantity, but this conclusion is so improbable that it seems rather to throw doubt on the validity of the method. Again, it was never possible to imitate exactly the current-voltage characteristic of the residual gas by means of any one of these gases alone. That gas is therefore probably a mixture—a conclusion likely enough, but one which makes it almost impossible to discover its composition by this method.

Attempts were also made to pump away and collect the residual gas. When a vessel is baked on the pump even to 120° C., the pressure in it is always notably higher than when it is cold; the evolution in these circumstances must be continuous. There is no difficulty in collecting gas from the high-pressure side of a diffusion pump connected to such a vessel, but there is great difficulty in proving that this gas comes entirely, or even mainly, from the baked vessel; some certainly comes from the connecting tubes (which cannot all be baked) and from the parts of the pump itself heated by the stream of mercury vapour. If, on the other hand, the gas is absorbed in cooled charcoal or even on cooled glass, there is very grave difficulty in ensuring that the gas liberated when the absorbent is heated is that which has been absorbed, neither more nor less. Much time was wasted on this work, and many methods which appeared satisfactory for a time had to be abandoned on further inquiry. The only conclusion that can be stated with confidence is, that in all experiments of this kind, water and carbon dioxide were always found in the gas collected, and both may therefore be present in the residual gas evolved from the heated vessel, while there was never certain evidence of the presence of any other gas from that source.

(6) *Discussion.*

Such are the facts; now some interpretation of them must be attempted. They are simplest when the vessels are metal coated. Here we may suppose that there is present in the vessel a definite quantity of gas, depending on the conditions prevailing during the deposition of the metal layers and on the maximum temperature to which it has since been heated. This gas is partially absorbed on the walls, the quantity so adsorbed increasing as the temperature falls. The clean-up increases this adsorption; its effect may be described, as in a previous paper *, as a decrease of the vapour-pressure of the adsorbed gas, the decrease being strictly permanent only while the discharge lasts.

All this is comprehensible and in accordance with ideas already put forward. The only important question which remains is why the clean-up reduces the vapour-pressure. Here the later work has neither increased nor decreased the difficulties encountered previously. The ionization of the gas must cause it to assume some state in which it adheres

* Research Staff of the G. E. C. *loc. cit.* p. 571.

more firmly to solid surfaces, but this state cannot be simply that of ionization.

But in the glass vessels the facts are not so simple. For here we have a truly permanent as well as a temporary effect of the clean-up. In the final state the conditions may be the same as in the metal-coated vessels ; there may be a definite quantity of gas present of which merely the adsorption is changed. But if so, why is this quantity of gas so nearly independent of the history of the vessel and especially of the quantity initially present ; if the clean-up can remove, gradually but permanently, so large a proportion of the initial gas, why can it not remove all? An answer may be suggested, athough it is admittedly speculative.

The permanent reduction of pressure must surely be due to some change in the state of the gas, involving the glass and possibly, though not certainly, the metal parts of the vessel, which is more permanent than adsorption ; let us call it by that term of convenient ambiguity, a chemical reaction. It is conceivable that only part of the gas initially present is capable of this reaction, which ceases when that part is exhausted ; but in view of the independence of the final on the initial pressure, another view seems much more probable. It is known * that some silicates at high temperatures in contact with water form water-silicate solutions characterized by definite equilibrium pressures of the vapour phase ; it is not unlikely that similar solutions are formed in which carbon dioxide replaces water. There is abundant evidence that diffusion is possible in glass at temperatures as low as 120° C. ; the glass is always in contact with water and carbon dioxide on the exterior surface ; the equilibrium pressure of the saturated solutions of water and carbon dioxide in glass will therefore establish itself on the inside. This pressure at T_a may be identified with the final p_a. If there is initially within the vessel more vapour than corresponds to the pressure, the discharge, in addition to increasing the adsorption, as in metal vessels, will remove some of it permanently by the chemical reaction ; but when the amount has reached that corresponding to the equilibrium pressure, any quantity removed by chemical reaction during (c) will be restored during the subsequent (a). On the other hand, p_b does not represent the equilibrium pressure at T_b for two reasons. First, the rate of diffusion doubtless increases enormously rapidly with the temperature ; the

* G. W. Morey, J. Am. Chem. Soc. xxxix. p. 1173 (1917).

temperature falls from T_a to T_b in a few minutes, and during this time diffusion has not time to establish equilibrium between the vapour phase and the interior of the glass. Second, since the pressure of the vapour on the outside of the vessel is much greater than that on the inside, the excess of vapour would not be transferred to the outside, even if infinite time were allowed ; the superfluous vapour would remain inside as a separate phase ; p_b represents the pressure exerted by this superfluous vapour after some of it has been adsorbed on the glass surface ; owing to the adsorption p_b is less than p_a, but it will increase with T_a and p_a, even though T_b remains unchanged.

The objections to the theory are obvious. The complete similarity between samples of glass so different in composition is striking. Again, according to this view, the difference between the glass and the metal vessels is threefold. Metals do not enter into the supposed chemical reaction; they do not dissolve the gas ; there is no diffusion through them. None of these differences are precisely what would be expected. Nor is it easy to get fresh confirmatory evidence. Of course an attempt might be made to prepare glass wholly free originally from dissolved gas and to prevent it from absorbing gas from the air by a vacuum jacket; but the experimental difficulties have so far deterred us from the attempt ; it must be remembered that the supposed equilibrium pressure at 200° C. is only 10^{-4} mm., and that the pressure in the vacuum-jacket must be permanently below this limit. The only confirmation that can be offered at present is a difference in the time required to reach the equilibrium pressure at any given temperature ; this time was distinctly less in the metal-coated vessels, a difference consistent with the view that in these diffusion within the walls plays no part.

(7) *Consequences for High Vacuum Technique.*

But whatever may be the explanation, there is no doubt that there is a difference between glass and metal-coated vessels, which may be most important for some practical purposes. Our observations indicate that it is impossible to make a vessel with bare glass walls in which the pressure will remain permanently as low as 10^{-6} mm. in such conditions as are likely to prevail in practice. The pressure can be reduced below this value by the clean-up ; by taking great care to avoid heating of the walls of the vessel by the discharge used for the purpose, pressures as low as 10^{-8} mm.

can thus be reached ; but a very moderate rise of temperature will restore the original value. On the other hand, by coating the walls with evaporated metal, and taking care that the pressure during the evaporation is as low as possible, it is quite easy to obtain vessels in which the pressure at 20° C. is permanently less than 10^{-7} mm. and not more than 10^{-6} mm. at 120° C.*

In fact, the impression prevailing in some quarters that metals are to be avoided in vessels in which the highest vacua are to be obtained, appears to be based on a misunderstanding. If metals are present, the gas on their surface adsorbed from the atmosphere must be removed (and also the gas in the interior if they are ever to be raised to a temperature at which this is likely to emerge). Now, this gas cannot be easily removed by baking the whole vessel, for a reason which these experiments disclose. The adsorption on a metal surface varies more rapidly with the temperature than that on a glass surface. When the vessel is hot, it will be filled with vapour coming from the glass ; the supply of this gas is inexhaustible ; and the resulting pressure at a given baking temperature depends mainly on the ratio of the area of the glass surface to the diameter of the tubes connecting the vessel to the pump. Unless this ratio is unusually small, the pressure in the vessel during baking at 400° will not be less than 10^{-4} mm., and usually will be considerably greater. As the vessel cools, this vapour tends to be adsorbed on the surface of the metal rather than that of the glass, and is evolved thence if the temperature of the metal rises in subsequent operations. The metal surface can be freed from gas only by making the metal hot while the glass is comparatively cold ; but it can be freed by that method with great ease.

An illustration of this process is afforded by the difficulty mentioned on p. 373. There is always a rise of pressure when the filament of the gauge is heated, because the metal portions of it have adsorbed gas during the cooling of the vessel which is liberated when they are warmed by the filament. In the gauges in which this rise was abnormally large, the metal parts were probably in an abnormally receptive state, for some reason that is not understood at present.

* Even the smallest of these values are much greater than those which other workers appear to have no difficulty in obtaining. References to pressures of 10^{-9} are common in the literature, and even 10^{-13} has been mentioned ; but it is never clear whether the vessels in which these pressures were found were sealed off from the pump.

Appendix.

The following table gives the chemical composition and some of the physical properties of the four glasses used in the experiments :—

Characteristics of Glasses used for Vessels.

		A.	B.	C.	D.
Chemical Composition (main constituents only)	SiO_2	56·5	62	72·0	72·0
	Al_2O_3	—	—	—	3·0
	PbO	30·0	20	—	—
	CaO	—	4	5·6	3·0
	MgO	—	—	3·0	—
	K_2O.....	5·2	9	1·0	4·6
	Na_2O	6·3	3	16·0	2·5
	B_2O_3	—	—	—	15·0
Softening temperatures (relative).....		420° C.	520° C.	550° C.	620° C.
Temperature at which resistivity is 10^7 ohm/cm.^{3}.....		350° C.	415° C.	185° C.	400° C.
Temperature at which resistivity is 10^5 ohm/cm.^{3}		480° C.	550° C.	330° C.	605° C.

XXXI. *A Bath for Observations at Lower Temperatures.* *By* W. H. Patterson *.

A BATH of which the temperature is easily controllable, so that it can be rapidly cooled, then slowly cooled further, heated or kept constant near a particular temperature, is useful for many experiments.

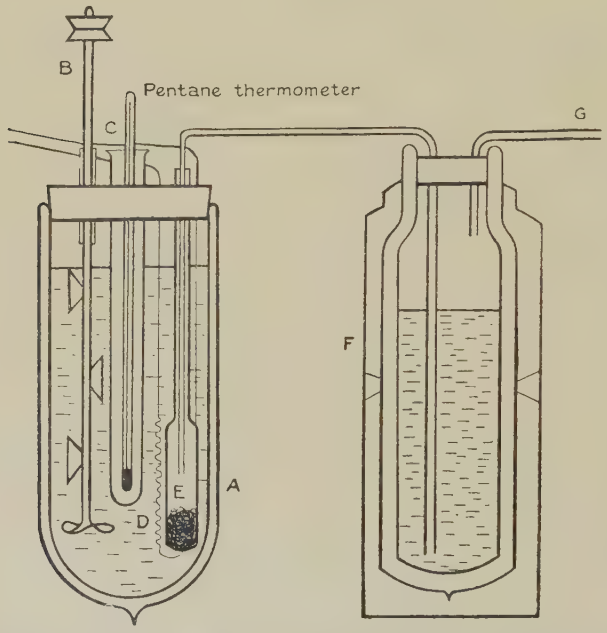
The apparatus described was designed for measuring the limits of miscibility of liquid pairs from room-temperature downwards. It has also been employed for determining "setting points" of many liquids, as a better control of purity than the tests usually made. In the latter case, the liquid to be tested is placed in the bath in a tube enclosed in a larger one with an air-space between, so that the pentane or other thermometer in the liquid may be sensible to the latent heat of change of state and indicate either the true "setting point," or, in the case of impure liquids, the "setting point range." While no novel principle is involved †, the apparatus is simple, it has a wide range, and even at the higher temperatures has many advantages over the use of ice or salt mixtures. It consists of a Dewar flask A, 11 × 4·5 cm., nearly filled with alcohol and provided

* Communicated by the Author.

† d'Arsonval, *C. R.* 133. p. 980 (1901), used a bath of paraffin cooled by allowing liquid air to drop into, and evaporate from, a small metal vessel placed on the surface, for maintaining temperatures −115° to −194° C.

with a cork through which pass a mechanical stirrer B and the tube for liquids to be tested C.

Connexions are made through the cork to a coil of about 50 cm. No 26 Eureka wire (the electrical resistance of which changes but little with the temperature). When the ends of the coil are connected to a single accumulator the rise of temperature of the bath is about $1^{\circ}{\cdot}5$ per minute. A two-way switch is provided for slower heating.



The cooling is effected by means of the tube E, which is wider at the lower end. At the bottom is a wad of cotton-wool. Into this tube passes a narrow glass tube with a fine orifice leading from the Dewar flask F which contains liquid air. The liquid air, in small amounts, is forced into E at will by means of a bicycle pump at G.

The apparatus has been used for temperatures between $+30^{\circ}$ and -120° C. A steady temperature is attained within half a minute of breaking the current or forcing over the liquid air. The temperature can be reduced, if desired, by 100 degrees in 15–20 minutes. Observations of the thermometer and liquids tested can readily be made through the walls of the Dewar flask, and it is only necessary to wipe off the moisture condensed on the outside occasionally, even at the lowest temperatures. The use of liquid air in the way described is very economical.

XXXII. *Molecular Association and the Equation of State.*

By M. F. Carroll, *M.Sc.* (*Lond.*)*.

In a recent paper by Prof. J. R. Partington and the author on the "Specific Heats of Carbon Monoxide and Hydrocyanic Acid Vapour" †, it was assumed from the measurements of Usherwood that hydrocyanic acid vapour is considerably associated to double molecules at the temperatures and pressures employed by Usherwood ‡ and the authors. Further, it was deduced that in the neighbourhood of the critical point, hydrocyanic acid consists almost entirely of double molecules; and since the critical constants of this compound have not yet been determined, use was made of certain empirical relations given by Walden § for calculating the critical data. Walden distinguishes between the so-called "normal" substances (such as hydrocarbons, ethers, etc.) and those described as "abnormal" (such as water, ammonia, acetic acid, and the alcohols), on the ground that certain physical properties of the "normal" compounds bear a simple and constant relation to each other, while the "abnormal" compounds show considerable divergence from this rule.

Similar evidence for this differentiation between "normal" and "abnormal" substances may be found in the variation of the constant f of van der Waals' vapour-pressure equation

$$\log P_c/p = f(T_c/T-1),$$

where f varies from about 1·8 to 4·0 for different substances. Thus in Landolt-Börnstein's tables the following classification is adopted:

Group 1.	$f < 2{\cdot}5$,	$RT_c/P_cV_c = 3{\cdot}0$ to $3{\cdot}5$
Group 2.	$f = 2{\cdot}6$ to $3{\cdot}2$,	$RT_c/P_cV_c = 3{\cdot}5$ to $4{\cdot}0$
Group 3.	$f > 3{\cdot}2$,	$RT_c/P_cV_c > 4{\cdot}0$,

where f is defined above and RT_c/P_cV_c is the ratio of the ideal to the actual value of RT at the critical point. Group 1 comprises the permanent gases, Group 2 the

* Communicated by the Author.
† Phil. Mag. xlix. p. 655 (1925).
‡ Journ. Chem. Soc. (T), ccxi. p. 1604 (1922).
§ *Zeit. phys. Chem.* lxvi. p. 385 (1909).

"normal" substances, and Group 3 the "abnormal" substances. Another criterion of abnormality is Trouton's rule,

$$\lambda/T = \text{a constant} = c,$$

where λ is the molecular latent heat of evaporation and T the absolute temperature. The constant c is approximately equal to 21·0 cals./deg. for the "normal" substances, and substances giving a higher value for c are regarded as associated, although acetic acid and its homologues, which are undoubtedly associated to a large extent, give a very low value for c, while a further class of substances corresponding to Group 1 of the above table, and which we will refer to as "subnormal" substances," give a very low value of c, ranging from 12·0 to 17·0 cals./deg.

The strongest evidence for this arbitrary division is found in the rule of Eötvös as modified by Ramsay and Young. The latter authors have shown that, in order to account for the deviation from the equation

$$d \cdot \gamma \frac{(Mv)^{2/3}}{dt} = \text{a constant} = -2{\cdot}11 \text{ approx.},$$

a greater molecular weight must be assigned to the "abnormal" substances than that obtained from vapour-density measurements. This equation is derived on the assumption that the "normal" substances are quite unassociated in the liquid state. Of late, however, this assumption has been questioned, although it appears to be generally accepted. A closer survey of the physical properties of the "normal" and "abnormal" substances shows that the division is quite arbitrary, the line of demarcation being very indefinite.

An attempt will now be made to show that association is common to all substances, and is quite appreciable even in the case of the gases of the inert group at low temperatures and high pressures. Although water and the alcohols are regarded as associated in the liquid state, it is usually assumed that in the gaseous state they are unassociated. This view is illogical, as may readily be seen from a consideration of the Cailletet-Mathias density-temperature curve. Thus, starting from water at its boiling-point and proceeding along the liquid-density curve, we should expect to find as the curve approaches the critical point that the degree of association becomes progressively less, since the volume increases. In the case of association to double molecules, the dependence of α, the degree of

association, upon the volume is given by the equation

$$\frac{\alpha^{\frac{1}{2}} V^{\frac{1}{2}}}{(1-\alpha)} = K,$$

where K is the association constant. Since the change is perfectly continuous, as is also the change from liquid to vapour at the critical point, we may reasonably assume that α decreases progressively with increase of volume; and proceeding thence along the vapour-density curve, we see that association should exist in the vapour at the boiling-point, or indeed under any conditions, and would in certain cases be given quantitatively by the above equation.

The only methods available for the absolute determination of association are a measurement of the vapour density of the gas and the various methods for estimating the molecular weight of dissolved substances. Only those substances are regarded as associated in the gaseous state which, like acetic acid and its homologues, give a vapour density considerably greater than the theoretical. Variations in the vapour densities of other substances are ascribed to deviation from the gas laws, and are accounted for by introducing into the ideal gas equation some function of P or V which will account for these deviations. So far all these equations of state, although showing good agreement in particular cases, are incapable of general application; so that of all the equations devised, whether theoretical or empirical, not one can be used to represent accurately the behaviour of fluids in general, or even that of any particular fluid over the entire range of its existence. If, however, molecular association is assumed to be quite general, it will be obvious that no known equation of state can represent accurately the behaviour of actual fluids. With regard to liquids, it appears to be still assumed quite generally that the molecular weight of a substance in the liquid state is necessarily the same as in the gaseous state—an assumption which is clearly unjustified. Such evidence as exists in its favour depends on the further assumption that the molecular weights of certain "normal" substances are identical under all conditions. The difficulty in establishing the existence of association in the vapours of the "normal" substances lies in the fact that the degree of association is so small that its effect on the vapour density is obscured by experimental error and by deviations from the gas laws. It should, however, be capable of approximate determination—provided sufficient accuracy can be obtained in the vapour density

measurements—by the use of a suitable equation of state which would represent exactly the deviations from the gas laws of an ideally "normal" substance—that is, a substance which possesses the same molecular weight under all conditions.

The Equation of State.

A discussion of the relative merits of the many equations of state which have been put forward from time to time is unnecessary in view of the attention which the subject has already received, and, in any case, only a few of these equations possess any real physical significance. Any equation purporting to account for the deviation of actual fluids from the ideal gas equation $PV=RT$ must take into consideration

(1) the attraction existing between the molecules;
(2) the finite size of the molecules;
(3) the finite time of contact.

The latter does not appear to have received the attention that it merits, but the effect of (1) and (2) has been treated exhaustively in most of the equations of state put forward, and of these the equation of van der Waals,

$$\left(P+\frac{a}{V^2}\right)(V-b)=RT,$$

is from the theoretical point of view the most attractive.

Applying the usual methods for the solution of this equation at the critical point, we find $RT_c/P_cV_c=s=8/3$ for all substances. The main objections to this equation are that a and b are not quite constant, and s is not constant and equal to 8/3, but varies from 3·1 for helium to about 5·0 for acetic acid. This variation is undoubtedly outside the range of experimental error, in view of the substantial agreement obtained by different observers for any given substance. This fact has been recognized by Guye, who expressed s as a function of the critical temperature, and other observers have modified the equation of state to allow for this and other variations. The conception of general association offers an explanation of this variation, as will be shown later.

The basic assumption made in the present theory is that the discrepancy between van der Waals' equation as applied to actual fluids and the true equation of state depends entirely upon *association*, and that for a completely non-associated substance van der Waals' equation holds rigidly—that is, a and b are constant and $s=8/3$. Association is defined in a

very broad sense. Thus, if we consider the effect of (3) from the standpoint of statistical dynamics, it will be obvious that the time of contact determines the number of molecules in a given volume. If the time of contact is not zero, it is possible that the substance is associated in the chemical sense (chemical combination) and groups of molecules are in contact for relatively long periods, or that the time of contact is small but finite, and oscillations about a centre of mass may occur before the molecules separate. This difference is clearly one of degree rather than of kind; hence both effects are included under the term "association." An ordinary substance, therefore, may be considered as an equilibrium mixture of unassociated molecules with the various products of association. If the degrees of association to 2, 3, or 4 molecules etc. are respectively α, β, γ, etc., one gram-molecule of an unassociated substance will give $(1-\alpha-\beta-\gamma-\ldots)$ unassociated molecules and $\left(\frac{\alpha}{2}+\frac{\beta}{3}+\frac{\gamma}{4}+\ldots\right)$ associated molecules. Therefore the number of molecules in equilibrium will be $\left(1-\frac{\alpha}{2}-\frac{2\beta}{3}-\frac{3\gamma}{4}-\ldots\right)$. The constant R of van der Waals' equation is proportional to the mean kinetic entropy of the molecules and is purely additive; hence, if R' is the absolute gas constant referred to N (Avagadro's constant) individual molecules,

$$R = R'\left(1-\frac{\alpha}{2}-\frac{2\beta}{3}-\frac{3\gamma}{4}-\ldots\right) = \frac{R'}{x},$$

where x is the ratio of the actual to the theoretical number of molecules. At the critical point this relation alone determines x for

$$\frac{R'}{x}\cdot\frac{T_c}{P_c V_c} = \frac{8}{3} \quad \text{and} \quad \frac{R' T_c}{P_c V_c} = s,$$

and therefore $x = 3/8s$.

It is not possible to state so precisely the effect of association on a the constant of molecular attraction, or on b the limiting molecular volume; but in general we may write

$$a = a' f_1(\alpha, \beta, \gamma, \ldots) \quad \text{and} \quad b = b' f_2(\alpha, \beta, \gamma, \ldots),$$

postulating only that a' and b' are constants and that the functions $f_1(\alpha, \beta, \gamma, \ldots)$ and $f_2(\alpha, \beta, \gamma, \ldots)$ involve no other variable than $(\alpha, \beta, \gamma \ldots)$. The modified van der Waals' equation then becomes

$$\left[P + \frac{a'}{V^2}\cdot f_1(\alpha, \beta, \gamma, \ldots)\right]\left[V - b' f_2(\alpha, \beta, \gamma, \ldots)\right] = f_3(\alpha, \beta, \gamma, \ldots) R' T.$$

If for simplicity we confine ourselves to association to double molecules, we have

$$\left[P+\frac{a'}{V^2}.f_1(\alpha)\right]\left[V-b'f_2(\alpha)\right]=\left(1-\frac{\alpha}{2}\right)R'T.$$

Following van Laar, we have for a and b

$$a=\left[a'(1-\alpha)^2+\sqrt{a'a''}\,.\,2\alpha(1-\alpha)+a''\alpha^2\right],$$

$$b=b'(1-\alpha)+b''\frac{\alpha}{2}.$$

The first expression may be more conveniently written

$$a=\left[\sqrt{a'}(1-\alpha)+\sqrt{a''}\frac{\alpha}{2}\right]^2,$$

where a' and b', a'' and b'' are the constants for the unassociated and associated molecules respectively. The simplest assumption we can make with regard to these constants is that $a''=2a'$ and $b''=\sqrt[3]{2b'}=b'/\cdot 631$, which gives for all sub-tances

$$a=a'(1-\cdot 293\alpha)^2 \quad \text{and} \quad b=b'(1-\cdot 369\alpha).$$

These expressions are probably too simple, and may vary with the nature of the substance. Quite good results have been obtained by their use, however, as will be shown later. Applying the usual methods for the evaluation of the constants of the equation in terms of the critical constants, we find

$$a'=\frac{a}{f_1(\alpha)}=\frac{3P_cV_c^2}{(1-\cdot 586\alpha+\cdot 086\alpha^2)},$$

$$b'=\frac{b}{f_2(\alpha)}=\frac{V_c}{3(1-\cdot 369\alpha)},$$

and

$$\frac{\left(1-\frac{\alpha}{2}\right)R'T_c}{P_cV_c}=\frac{8}{3}, \quad \text{or} \quad \frac{R'T_c}{P_cV_c}=s=\frac{8\left(1-\frac{\alpha}{2}\right)}{3},$$

from which α and therefore a' and b' may be calculated. The values of α, a', and b' calculated from the critical data are given in Table I. Columns 2 to 4 contain the most recent values of the critical data given in Landolt-Börnstein's tables. Column 5 contains the value of s, and columns 6 to 8 the values of α_c, a', and b' calculated therefrom. Column 9 contains the values of the association constant K_c given by the expression

$$K_c=\frac{\alpha_c^{\frac{1}{2}}V_c^{\frac{1}{2}}}{(1-\alpha_c)}.$$

Column 10 contains the ratio of the limiting volume to the

TABLE I.

Substance.	T_c° abs.	P_c. atmos.	V_c. c.c.s.	s.	α.	$a' \times 10^{-6}$.	b'. c.c.s.	K_c.	b'/V_c.
Hydrogen	33·2	12·8	69·68	3·038	·244	·2165	25·53	5·46	·231
Helium	5·2	2·3	61·55	3·082	·269	·0282	22·80	5·57	·233
Argon	150·7	50·0	75·15	3·293	·380	1·074	29·13	8·62	·244
Nitrogen	126·0	33·5	90·07	3·431	·445	1·076	35·91	11·42	·251
Oxygen	154·9	49·7	74·42	3·437	·448	1·095	29·72	10·47	·252
Methane	190·2	45·6	98·56	3·473	·464	1·783	39·63	12·62	·253
Carbon monoxide	134·4	34·6	90·03	3·542	·494	1·152	36·67	13·19	·257
Xenon	289·7	58·2	113·2	3·611	·522	3·268	46·77	16·10	·261
Carbon dioxide	304·4	72·9	94·84	3·615	·525	2·751	39·22	14·86	·261
Sulphur dioxide	430·2	77·7	124·7	3·646	·537	5·109	57·82	17·68	·262
Carbon tetrachloride	556·3	45·0	276·2	3·675	·548	14·65	115·3	27·22	·263
i-Pentane	460·9	32·9	307·3	3·741	·574	13·52	129·9	31·23	·266
Benzene	561·6	47·9	256·2	3·759	·581	13·72	108·6	29·12	·267
n-Pentane	470·3	33·0	309·8	3·771	·585	13·87	131·7	32·49	·267
Fluor-benzene	559·7	44·6	271·4	3·797	·595	14·48	116·0	31·37	·269
Ethyl ether	466·9	35·6	281·9	3·819	·603	12·54	120·8	32·86	·270
Methyl acetate	506·8	46·3	227·5	3·948	·645	10·96	99·5	34·13	·271
Ethyl acetate	523·2	38·0	286·1	3·952	·650	14·28	123·7	39·01	·272
Nitric oxide	177·1	64·0	57·25	3·966	·655	·967	25·17	17·76	·277
Ethyl alcohol	516·2	63·0	167·0	4·029	·676	8·179	74·22	32·29	·280
Ammonia	405·6	112·3	71·91	4·124	·707	2·733	32·44	24·32	·284
Methyl alcohol	513·0	78·5	117·6	4·563	·832	5·707	56·57	58·57	·303
Water	638·0	200·5	54·71	4·784	·885	2·751	27·04	60·46	·311

critical volume, a value which increases with the degree of association. Assuming that association only takes place to double molecules, the limiting volume is therefore equal to the volume of the double molecules, which is found by putting $\alpha = 1$ in the expression given on p. 390, whence

$$b'' = \cdot 631 b' \quad \text{and} \quad \frac{b''}{V_c} = \frac{\cdot 631 b'}{V_c} = \frac{1}{3} \cdot \frac{\cdot 631}{(1 - \cdot 369 \alpha_c)}.$$

The mean value from Table I. is approximately ·260, which is the value obtained by D. Berthelot * by extrapolating the Cailletet-Mathias mean density line to the absolute zero. No great reliance can be placed on this criterion, however, since we are in doubt as to the validity of the extrapolation, and, besides, we have no reason to assume that all substances are completely associated at the absolute zero. Indeed, conceding the first point, we may explain the variation in the values of b''/V_c by assuming that the simpler substances are less completely associated, and the more complex substances are further associated to triple molecules etc. at the absolute zero.

Table I. contains only those values of the critical constants for which reasonable agreement has been obtained by different observers, and it is assumed for the sake of comparison that association only proceeds to the second stage, which, as will be shown later, is not strictly true, especially in the case of the "abnormal" substances. The examples given in the table may be divided roughly into the three classes mentioned above—from hydrogen to carbon monoxide "subnormal," from xenon to ethyl acetate "normal," and from nitric oxide to acetic acid "abnormal" substances; but, as previously pointed out, this division is purely arbitrary, as will be seen by following the values of s from ethyl ether to methyl alcohol and observing the gradual transition from "normal" to "abnormal" substances.

Young's work, from which most of the data are taken, was mainly confined to the "normal" substances, the physical properties of which fall within very narrow limits—a fact which has given rise to many empirical relations which are entirely unsuccessful outside this range.

The equation of state can now be used to calculate the degree of association in both the liquid and gaseous state at any temperature and pressure. Thus, on any given isotherm,

* *Arch. Neer.* (2) v. p. 466 (1900).

since the association constant K_v is a function of temperature only, it should be constant for all values of P and V on the isotherm. Tables II. to IV. contain the values of α and K_v calculated for some representative substances. The degree of association was calculated by substituting successive values of α in the equation of state until a value which satisfied the equation was found. The value of the association constant was then calculated, assuming that the law of mass action holds under these conditions.

TABLE II.

Hydrogen *.

$T = 273°$ abs. $a' = 2{\cdot}165 \times 10^5$. $b' = 25{\cdot}53$ c.c.s.

P atmos.	V c.c.s.	α.	K_v.
100	239·6	·0184	2·14
150	164·4	·039	2·64
200	127·4	·056	2·83
400	71·9	·134	3·58
600	53·48	·216	4·34
800	44·21	·290	4·98
1000	38·56	·363	5·87

TABLE III.

Carbon Dioxide *.

$a' = 2{\cdot}751 \times 10^6$. $b' = 39{\cdot}22$ c.c.s.

$T = 323°$ abs.				$T = 373°$ abs.			
P atmos.	V c.c.s.	α.	K_v.	P atmos.	V c.c.s.	α.	K_v.
50	421·5	·170	10·10	50	540·9	·061	6·12
100	110·1	·387	10·64	100	230 9	·132	6·36
125	70·84	·454	10·41	125	169·8	·165	6·34
150	62·62	·467	10·25	150	131·2	·191	6·19
200	56·06	·480	9·97	200	91·33	·241	6·18
400	47·72	·487	9·40	400	58·19	·345	6·84
600	44·34	·494	9·25	600	51·01	·381	7·12
1000	40·66	·520	9·58	1000	44·82	·428	7·65

* Amagat, *Ann. Chim. Phys.* (5) xxix. p. 68 (1898).

Table IV.

Ethyl Ether *.

$a' = 1{\cdot}254 \times 10^7$. $b' = 120{\cdot}8$ c.c.s.

$T = 470°$ abs.

P atmos.	V c.c.s.	α.	K_v.
13·29	2454	·156	23·16
11·80	2817	·143	23·42
9·62	3540	·128	24·41
8·114	4262	·116	25·16
7·049	4982	·1028	25·23
6·207	5702	·0930	25·40
5·551	6419	·0905	26·51
5·027	7137	·0852	26·96

It will be seen from the above tables that fairly good agreement is obtained for carbon dioxide and ether, but the value of K_v for hydrogen shows a marked variation. Closer agreement can hardly be expected in view of the inaccuracies inherent in the determination of the critical data on which are based the values of a' and b', and consequently the values of α and K_v. The small differences in the results for the critical constants obtained by different observers are sufficient to cause appreciable error in the value of α; hence the exact application of the equation of state must depend on very accurate determinations of the critical data.

The equation of state can also be used to calculate the value of α and K_v on the vapour-pressure curve for both the liquid and gaseous phases. At any given point on the curve, K_v should be identical for both phases, or

$$\frac{\alpha_g^{\frac{1}{3}} V_g^{\frac{1}{3}}}{(1-\alpha_g)} = \frac{\alpha_l^{\frac{1}{3}} V_l^{\frac{1}{3}}}{(1-\alpha_l)} = K_v.$$

The values of α and K_v on the vapour-pressure curve for various substances have been calculated, and a selection of the results are given in Tables V. to VIII. The degree of association-temperature curve for carbon tetrachloride and isopentane has been plotted, and is shown in the accompanying diagram.

* Ramsay & Young, Phil. Mag. xxiii. p. 435 (1877).

Fig. 1.—Degree of Association-Temperature.

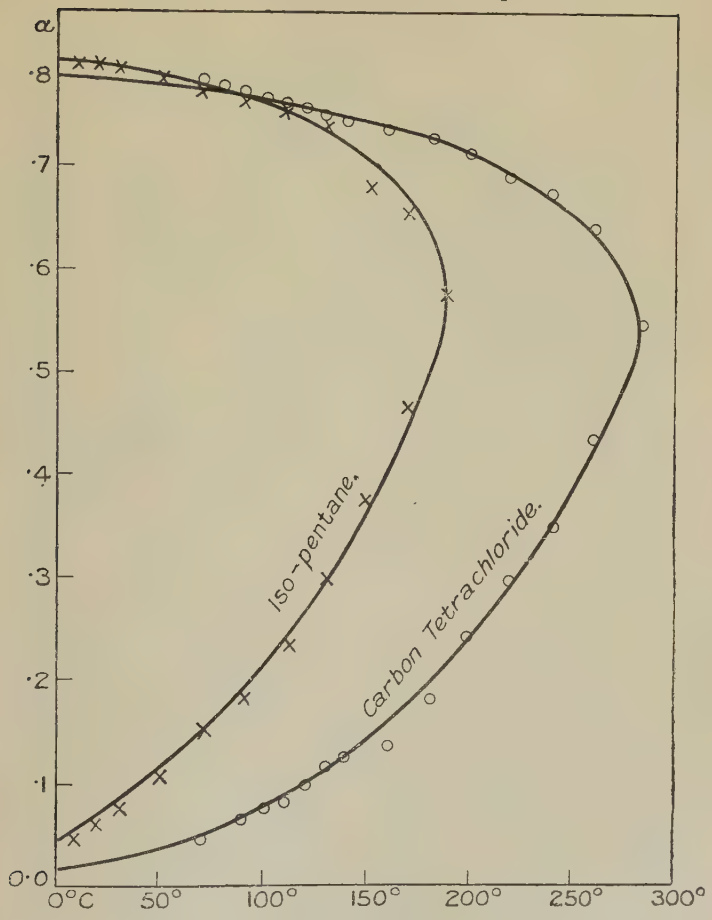


TABLE V.

Carbon Dioxide *.

$a' = 2{\cdot}751 \times 10^6$. $b' = 39{\cdot}22$ c.c.s.

$T°$ abs.	P atmos.	V_l c.c.s.	V_g c.c.s.	a_l.	a_g.	K_l.	K_g.
273	34·3	48·15	458·2	·672	·293	17·34	16·39
278	39·0	49·56	346·8	·661	·336	16·89	17·15
283	44·2	51·40	330·9	·651	·352	15·58	16·65
288	50·0	54·06	278·5	·630	·387	15·75	16·93
293	56·3	57·45	231·6	·611	·420	15·21	17·00
298	63·3	62·59	183·3	·578	·470	14·33	17·52
303	70·7	73·58	131·7	·541	·514	13·75	16·93
304·4	72·9	94·84		·525		14·86	

* Amagat, *loc. cit.*

Table VI.

Benzene *.

$a' = 1{\cdot}372 \times 10^7$. $b' = 108{\cdot}6$ c.c.s.

$T°$ abs.	P atmos.	V_l c.c.s.	V_g c.c.s.	a_l.	a_g.	K_l.	K_g.
343	·511	94·58	38230	·817	·0234	48·03	30·65
353	·992	95·76	28550	·814	·0228?	47·46	26·20
363	1·337	96·94	21610	·811	·0302	46·91	26·34
373	1·769	98·40	16580	·808	·0456	46·44	28·81
393	2·944	101·4	10160	·795	·0868	43·80	32·53
423	5·705	106·7	5429	·777	·120	40·83	28·97
443	8·387	110·9	3737	·770	·144	40·17	27·07
473	14·03	118·3	2200	·752	·213	38·00	27·51
503	22·13	128·6	1305	·724	·314	34·96	29·51
533	33·39	146·4	754·4	·675	·444	30·59	32·92
561·6	47·9	256·2		·581		31·23	

Table VII.

Carbon Tetrachloride †.

$a' = 1{\cdot}465 \times 10^7$. $b' = 115{\cdot}3$ c.c.s.

$T°$ abs.	P atmos.	V_l c.c.s.	V_g c.c.s.	a_l.	a_g.	K_l.	K_g.
343	·808	102·9	33700	·782	·0425	41·14	39·53
353	1·110	104·3	25310	·777	·0316?	40·37	—?
363	1·463	105·8	19330	·772	·0630	39·65	37·27
373	1·917	107·4	15000	·766	·0746	38·75	36·23
383	2·479	109·0	11790	·760	·0838	37·93	34·31
393	3·147	110·8	9396	·756	·0992	37·51	33·89
403	3·950	112·6	7560	·750	·1136	36·76	33·07
413	4·901	114·5	6160	·746	·1250	36·39	31·61
433	7·288	118·6	4319	·737	·1362	35·55	27·75
453	10·40	123·5	2941	·728	·180	34·85	28·02
473	14·39	129·5	2075	·714	·241	33·62	29·46
493	19·47	137·3	1481	·692	·295	31·64	29·65
513	25·83	147·4	1052	·674	·350	30·59	29·52
533	33·58	163·7	717·6	·639	·434	28·35	31·18
556·3	45·0	276·2		·548		27·22	

* Young, Proc. Roy. Soc. Dubl. (n. s.) xii. p. 374 (1910).
† Young, *loc. cit.*

TABLE VIII.

Isopentane *.

$a' = 1{\cdot}352 \times 10^7$. $b' = 129{\cdot}9$ c.c.s.

$T°$ abs.	P atmos.	V_l c.c.s.	V_g c.c.s.	a_l.	a_g.	K_l.	K_g.
283	·514	114·4	43700	·800	·0450	47·84	46·44
293	·754	116·2	30530	·797	·0594	47·67	45·28
303	1·073	118·1	21810	·793	·0782	46·49	45·34
323	2·017	122·4	12070	·784	·1068	44·42	40·19
343	3·489	127·3	7120	·773	·1502	43·72	38·50
363	5·563	133·0	4453	·765	·1814	42·92	34·72
383	8·679	140·1	2865	·754	·234	41·78	33·79
403	12·77	149·1	1879	·741	·297	37·04	34·43
423	18·17	162·0	1234	·680	·371	32 80	34·02
443	25·13	184·0	771·1	·654	·464	31·71	35·29
461	32·96	307·3		·574		31·22	

Quite good results are obtained for carbon tetrachloride, carbon dioxide, and isopentane; but the divergence due to further association becomes appreciable in the case of benzene, ether, and alcohol, the latter giving a value of $\alpha = {\cdot}92$ at the boiling-point, assuming simple association only. With water and acetic acid the effect of further association is more marked, and on calculating the degree of association for these substances on the above assumption a value of $\alpha > 1{\cdot}0$ is obtained. Attempts to evaluate the first and second degree of association α and β for these substances present considerable difficulties, but approximate methods of calculation give for water a value of $x = 2{\cdot}3$ and for acetic acid $x = 3{\cdot}0$ at the boiling-point. It is probable also that association proceeds to the second stage even in the case of the simpler compounds given above, but the effect is relatively small and does not cause any serious error below $\alpha = {\cdot}70$. Above this the effect of further association becomes apparent. It is for this reason that such emphasis has been placed on the results for carbon tetrachloride, the simplest of the thirty organic compounds investigated by Young. The degree of association of this compound is only ·548 at the critical point, and the values of K_l and K_g show very good agreement. The effect of discrepancies in the experimental data is seen in Table VII. The vapour-pressure of carbon tetrachloride at 353° abs. is not given in Young's paper; hence the value given by Regnault † was used instead. The divergence is quite marked, as will be seen from the value of α at this

* Young, *loc. cit.*

† *Mém. des Paris*, xxvi. p. 339 (1860).

temperature. As would be expected, the values of K show a more regular decrease than the values of K_g, since a determination of the volume of the vapour is attended by greater difficulties and is more liable to error than a determination of the volume of the liquid. Also the value of α_l is not so seriously affected by inaccuracies in the vapour-pressure determination as is the value of α_g. Hence, in the calculation of the heat of association Q_v, only the values of K_l have been used. In the case of carbon dioxide the temperature range is too small to give even an approximate estimate of the heat of association; but good agreement is obtained for the other examples given above if the values of α_l are used and Q_v calculated over a temperature range of at least 100° C. Table IX. contains the values of Q_v for carbon tetrachloride calculated from the formula

$$Q_v = 4{\cdot}571 \log_{10} \frac{K_1}{K_2} \cdot \frac{T_2 T_1}{T_2 - T_1}$$

over the temperature range stated.

Table IX.

Temperature range, ° abs.	Q_v cals.	Mean Q_v cals.
343–443	478·2	
353–453	467·0	
363–463	467·7	478·4
373–473	497·5	
383–483	481·0	

As in the above table, Q_v is fairly constant for all the substances investigated between the boiling-point and the critical point; but a slight increase with temperature is shown and is to be expected, since, in general, Q_v is a function of the absolute temperature. No attempt has been made to allow for this variation, as the values of K_l are not considered to be sufficiently accurate to admit of more exact calculation.

In all cases investigated up to the present it has been found that Q_v increases with temperature, but is approximately constant and equal to 500 cals. for the "normal" substances between the boiling-point and the critical point. For the "subnormal" substances it is very much less: *e.g.* for nitrogen, $Q_v = 79$ cals. In general, Q_v increases with the complexity of the molecule.

The Latent Heat of Evaporation.

A further test of the equation of state consists in the calculation of the latent heats of evaporation from values of P and V on the vapour-pressure line.

Maxwell's theorem gives the relation *

$$P(V_g - V_l) = \int_{V_l}^{V_g} p \,.\, dV. \quad . \quad . \quad . \quad . \quad (1)$$

Substituting in the equation the expression for p derived from the equation of state, we have

$$\int_{V_l}^{V_g} p \,.\, dV = \int_{V_l}^{V_g} \frac{\left(1-\frac{\alpha}{2}\right) RT}{(V-b)} \,.\, dV - \int_{V_l}^{V_g} f_1(\alpha)\, \frac{a'}{V^2} \,.\, dV \quad (2)$$

$$= \int_{Vl}^{V_g} \frac{R'T}{V-b} \,.\, dV - \int_{V_l}^{V_g} \frac{\alpha R'T}{2V} \,.\, dV$$

$$- \int_{V_l}^{V_g} \frac{a'}{V^2} f_1(\alpha) \,.\, dV. \quad . \quad . \quad (3)$$

Neglecting the variation of b with α, and substituting dV in terms of α,

$$dV = K^2 \frac{(\alpha^2-1)}{\alpha^2} d\alpha. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$\therefore \int_{V_l}^{V_g} p \,.\, dV = \int_{V_l}^{V_g} \frac{R'T}{V-b} \,.\, dV + \int_{a_l}^{a_g} \frac{R'T}{2} \cdot \frac{1+\alpha}{1-\alpha} d\alpha$$

$$+ \frac{a}{K^2} \int_{al}^{a_g} \frac{1+\alpha}{(1-\alpha)^3} \cdot (1 - \cdot 586\alpha + \cdot 086\alpha^2)\, d\alpha, \quad . \quad (5)$$

which gives on integration the expression :

$$P(V_g - V_l) = R'T \left[\log \frac{(V-b)_g}{(V-b)_l} - \log \frac{(1-\alpha)_g}{(1-\alpha)_l} + \frac{\alpha_l - \alpha_g}{2} \right]$$

$$+ \frac{a}{K^2} \left[\frac{1}{2} \left(\frac{1}{(1-\alpha_l)^2} - \frac{1}{(1-\alpha_g)^2} \right) - \cdot 328 \left(\frac{1}{(1-\alpha_l)} \right.\right.$$

$$\left.\left. - \frac{1}{(1-\alpha_g)} \right) + \cdot 242 \log \frac{(1-\alpha)_g}{(1-\alpha)_l} \right] . \quad . \quad . \quad . \quad (6)$$

From the Clausius-Clapeyron equation,

$$\lambda = T \frac{dP}{dT} (V_g - V_l),$$

$$\lambda = R'T \left[\log \frac{(V-b)_g}{(V-b)_l} - \log \frac{(1-\alpha)_g}{(1-\alpha)_l} + \frac{\alpha_l - \alpha_g}{2} \right]$$

$$+ \frac{2aQ_v}{K^2 R'T} \left[\frac{1}{2} \left(\frac{1}{(1-\alpha_l)^2} - \frac{1}{(1-\alpha_g)^2} \right) \right.$$

$$\left. - \cdot 328 \left(\frac{1}{(1-\alpha_l)^2} - \frac{1}{(1-\alpha_g)^2} \right) + \cdot 242 \log \frac{1-\alpha_g}{1-\alpha_l} \right], \quad (7)$$

on differentiating the expression for $P(V_g - V_l)$ with respect to T.

* *Cf.* Partington, 'Chemical Thermodynamics,' 1st edit. pp. 231, 349.

From this expression, λ can be calculated and compared with the value obtained experimentally and with the value calculated from the vapour-pressure equation. In the differentiation of (6), Q_v has been assumed constant, whereas, as previously pointed out, it varies with the temperature. It would have been more accurate to have used the expression

$$Q_v = Q_0 - aT.$$

This, and the assumptions involving the term $(V-b)$, account for the discrepancies between the calculated and experimental results. The results for carbon tetrachloride and benzene are given in the following tables:—

TABLE X.

Carbon Tetrachloride.

$Q_v = 478{\cdot}2$ cals. $\quad a' = 1{\cdot}465 \times 10^7$.

$T°$ abs.	a_l.	a_g.	K_l.	λ cals.	λ cals. (Young).
343	·782	·0425	41·14	7450	7210
353	·777	·0316	40·37	7200	7090
363	·772	·0630	39·65	7010	6955
373	·766	·0746	38·75	6800	6800
393	·756	·0992	37·51	6400	6479
413	·746	·125	36·39	5980	6148
433	·737	·136	35·55	5570	5843
453	·728	·180	34·85	5150	5451
473	·714	·241	33·62	4740	5020

TABLE XI.

Benzene.

$Q_v = 618{\cdot}8$ cals. $\quad a' = 1{\cdot}372 \times 10^7$.

$T°$ abs.	a_l.	a_g.	K_l.	λ cals.	λ cals. (Young).
363	·811	·0302	46·91	7870	7310
373	·808	·0456	46·44	7560	7130
393	·795	·0868	43·80	7035	6760
423	·777	·120	40·83	6470	6300
473	·752	·213	38·00	5330	5368

Empirical Relations.

A comparison of the value of x—the ratio of the actual molecular weight to the ideal molecular weight—at the boiling-point shows that, as far as can be determined at present, the ratios x_g/x_c and x_l/x_c are approximately constant

for all substances. In other words, the law of corresponding states applies also to the degree of association. Hence any law or rule which has for its basis the law of corresponding states should also include some reference to the degree of association. Thus, with Trouton's rule, the "normal" substances which give a constant approximately equal to 21·0 cals./deg. are precisely those which have approximately the same reduced molecular volume and molecular ratio x at the boiling-point, and the other constants in the latent heat equation (7) are also approximately equal. Therefore Trouton's rule should be modified to include some function of α. In this connexion it is interesting to note that Longuinine* shows that, if in the case of the fatty acids he double molecular weight is used in calculating $\lambda = ML$, the same value is obtained for the constant in Trouton's expression as for the "normal" substances. This may be expressed by writing

$$\frac{\lambda}{T} \cdot \frac{1}{x} = C,$$

where x is defined above. This correction is, however, too empirical, and any attempt to modify Trouton's rule must take into account some function of α for both the liquid and gaseous state.

The rule of Eötvös may be treated in a similar manner. Thus the "normal" substances give a value for the constant $A = -2{\cdot}11$. If, however, we allow for association, we have

$$\frac{d \,.\, \gamma(Mv \,.\, x)^{2/3}}{dT} = A.$$

Substituting a mean value of $\alpha = {\cdot}80$ for the "normal" substances at the boiling-point, we find for the ideal associated state:

$$\frac{d \,.\, \gamma(Mv)^{2/3}}{dT} = -2{\cdot}44.$$

If we select water as typical of the associated substances, we find from the rule of Eötvös that at the boiling-point $x = 1{\cdot}7$ approximately. Using the value $A = 2{\cdot}44$, we find $x = 2{\cdot}1$ approximately, whereas the value of x deduced from the law of corresponding states is about 2·3. This assumes that x does not vary appreciably over the range used in

* *Ann. Chem. Phys.* xiii. p. 289 (1898).

calculating the constant of the expression, but, as shown in the tables above, this assumption is true over a range of about 10–20° C.

The application of the equation of state to the calculation of the degree of association of the "abnormal" substances must be deferred until the variation of the constants a and b of van der Waals' equation, with the degree of association, has been further investigated and placed on a more exact basis.

The author is indebted to Mr. J. B. P. Harrison, F.I.C., and Mr. A. L. Bloomfield, B.A., B.Sc., of these laboratories, for valuable criticisms and suggestions.

The Research Laboratories,
A. Boake, Roberts & Co. Ltd.,
Stratford, E. 15.

XXXIII. *Phase-effect and the Localization of Sound: an Examination of the Myers-Wilson Hypothesis.* By H. Banister, *B.Sc.* (*Lond.*), *Ph.D.* (*Cantab.*), *St. John's College, Cambridge* *.

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Appendix.

I. Introduction.

1. ALTHOUGH, as I have pointed out in a previous paper*, Myers and Wilson were not the first to suggest that the "phase-effect" might be due to binaural differences of intensity brought about by bone conduction across the head, yet, since their statement of the hypothesis covers practically the whole field, and since the hypothesis is most generally, at least in English-speaking countries, associated with their names, it seemed appropriate that their account should form the basis of this inquiry.

II. The Myers-Wilson Hypothesis.

2. Myers and Wilson found that one sound was heard when the ears were stimulated separately and simultaneously by similar sound-waves of a given frequency; and that the localization of this sound depended on the relative phases of the vibrations at the ears.

3. They considered it very hard to believe that the phase differences were appreciated directly †, and suggested that the localization was actually based on subjective differences of intensity. They further showed that these differences of intensity might be objective to the inner ear, if certain assumptions were made.

* Phil. Mag. July 1926, p. 144.
† Brit. Journ. Psych. ii. p. 378 (1908).

III. Purpose of the Paper.

4. In this paper I propose to examine their hypothesis. First, I shall discuss the assumptions on which the hypothesis is based, and then I shall consider deductions from the hypothesis which can be tested experimentally.

IV. An Examination of the Assumptions on which the Myers-Wilson Hypothesis is based.

(a) *The three fundamental assumptions.*

5. Myers and Wilson base their hypothesis on the three following assumptions * :—

(*a*) The sound entering one ear is transmitted through he bones of the head to the internal ear on the opposite side.

(*b*) The retardation in phase, due to this ear to ear conduction, is small.

(*c*) The two (direct and transmitted) sets of waves, at their meeting in one or other ear, arrive from opposite directions.

(b) *The first assumption.*

6. I have, in a previous paper [1] considered the evidence for the assumption that sound may be transmitted through the head, and it is therefore not necessary to enlarge on it here.

7. The conclusions reached were that there is no trustworthy evidence that aerial sound-waves, of normal intensity, exciting one ear, can be transmitted through the head to the other ear. The only direct evidence for bone conduction was obtained twenty-five years ago with dead heads [2]. More recent experiments [3] have produced negative results, showing that the amount of sound energy which could enter the head was too small to be appreciated. Indirect experiments [4], [5], [1] are against the assumption. If there were transmission of sound through the head, it would still remain to be shown that the transmission was due to bone conduction. It might, with perhaps more plausibility, be set down to transmission through the sinuses of the head.

* Brit. Journ. Psych. ii. p. 378 (1908).

(1) Phil. Mag. July 1926, p. 144.

(2) Mader, *Sitzungsber. d. Kais. Akad. d. Wissens. Wien*, cix. pp. 37–75 (1900).

(3) Nikiforowsky, *Zeit. f. Sinnes Physiol.* xlvi. pp. 179–197 (1912).

(4) Cross & Godwin, Amer. Acad. Arts & Sci. n. s. xix. pp. 1–12 (1891).

(5) Peterson, Psych. Rev. xxiii. pp. 333–351 (1916).

8. So, though there is ample evidence that, *if* sound vibrations are set up in the bone of the head, they are conducted to the ears, there is no evidence, at present, to substantiate Myers and Wilson's assumption * that

> "it is impossible to stimulate the end organs of one ear without at the same time stimulating those of the other ear by bone conduction."

(c) *The second assumption.*

9. The second assumption (that the retardation in phase, due to this ear to ear conduction, is small) may be accepted if the first assumption (that there is ear to ear "bone conduction") is granted, for the velocity of the transmission of sound is very much greater in bone than in air.

10. If, however, there is transmission through the head, and if the transmission is through the sinuses and cavities of the head, the retardation of phase would very possibly be large, for the velocity of transmission through narrow tubes is much slower than in the open air.

11. But whether the retardation is large or small, the hypothesis is not substantially affected. If there is transmission through the head from one ear to the other, and if the rate of transmission through the head is different from that in the open air, the hypothesis in general holds. If the rate of transmission through the air is such that the phase retardation is between π and 2π, no change of sign, which is the essence of the third assumption, need be postulated; if the phase retardation due to the transmission through the head is less than π, the change of sign is necessary. I shall demonstrate the truth of this later (para. 30).

12. At the same time, as Rayleigh pointed out in 1909 †, there will be no retardation

> "if we are to suppose that the framework of the skull is thrown into vibration by sounds which enter by either ear"

unless we appeal to "viscous effects," when it "becomes a question whether the propagation across the head .... would suffice" to produce the effects observed.

(d) *The third assumption.*

13. The third assumption—that the direct and transmitted sets of waves, at their meeting, arrive from opposite

* Brit. Journ. Psych. ii. p. 380 (1908).
† Proc. Roy. Soc. lxxxiii. A, pp. 61-64 (1909); Scientific Papers, v. p. 524.

directions—is more difficult to accept, or to criticize, because the manner in which the vibrations are supposed to be set up in the bone at one side, and finally handed on to the end organs at the other side, is not stated. The assumption is, admittedly *, made to suit the facts; but its validity is strongly stated †. No physiologist

> "will maintain that the vibrations which are thus conducted, say, from the left ear across the head, reach the end organs of the right ear by passing to the temporal, parietal, and occipital bones, which cover the right side of the skull, and that they then turn in towards the right inner ear by way presumably of the drum and ossicles, now accompanying the vibrations which travel to the right ear directly. There can be little doubt that the direct route is the only one which it is worth while to consider, the vibrations passing from one ear at once to the petrous portion of the opposite temporal bone in which the auditory end organs of that side are lodged."

14. Now, Foster ‡ states as follows :—

> "That the vibrations which thus [by bone conduction from a fork held between the teeth] reach the internal ear are, for the most part, at least, conducted through the tympanum, and not brought to bear on the perilymph directly through the bony walls of the labyrinth, is not only indicated by the effect just mentioned of closing the meatus, for this could have no influence on the labyrinth itself, but may be also proved by experiment. If a style be attached to a stapes laid bare in the skull, the vibrations of a tuning-fork brought into contact with the skull will lead to corresponding movements of the style."

15. It will thus be seen that one physiologist considered that sounds heard by bone conduction were communicated to the ear *viâ* the tympanic membrane, while later physiologists, *e. g.* Bezold and Liebenmann §, held the same view. If the vibrations are communicated by the direct route, how are they to be supposed to act on the end organ? The mechanism of the bone conduction has not been outlined by Myers and Wilson with the fullness which is necessary for

* Proc. Roy. Soc. lxxx. A, p. 265 (1908).
† Brit. Journ. Psych. ii. p. 383 (1908).
‡ 'Text-Book of Physiology,' 1891, p. 1332.
§ 'Text-Book of Otology,' 1908.

any close criticism. One criticism was raised by Rayleigh *, who pointed out in 1909 that the assumption, that two vibrations arriving at the inner ear from opposite directions co-operate if the phases are opposite and tend to neutralize one another if the phases are the same, is

> "justified if the effect depends upon the velocity of vibration, as when aerial waves impinge from opposite directions upon a sensitive flame. But if the question were the effect upon a resonator of the kind employed by Helmholtz, the direction of travel is indifferent, and co-operation, in all cases, required that the phases be the same."

16. The change of phase was, it would appear, introduced because the vehicle of the transmission through the head was supposed to be bone conduction. If the retardation of the transmitted wave is small—less than π—this change of phase is necessary, otherwise the result of assuming transmission would make the sound loudest at the ear which lags in phase. If, however, the retardation is between π and 2π, no change of phase is necessary. For a complete examination of the hypothesis we should consider the more generalized case, assuming that there is transmission through the head, and taking account of the two alternatives, when the retardation due to the transmission through the head is greater or less than π.

(e) *Sensitivity to binaural differences of intensity produced by cross conduction.*

17. Myers and Wilson appear to consider that the binaural differences of intensity produced by the cross-conducted sounds are small, for they quote two experiments † to show that we are "extraordinarily sensitive" to such differences of intensity.

18. The first experiment is the well-known one due to Weber, which they describe as follows:—

> "If a vibrating tuning-fork be placed on the vertex of the skull, its tone will be localized somewhere midway between the two ears. But if a finger be introduced into one auditory meatus, the apparent position of the tone is at once changed. It is localized on the same side as the auditory meatus into which the finger has been introduced."

* Proc. Roy. Soc. lxxxiii. A, p. 524 (1909).
† Brit. Journ. Psych. ii. p. 381 (1908).

19. The experiment does not, in my opinion, prove any extraordinary sensitivity. The physical effect of closing the meatus is at present very conjectural; while the psychological effect has not, so far as I am aware, been studied at all. But, ignoring any psychological factors, and confining our attention to the physical, I do not see how the effect could be a small one or one requiring any *extraordinary* sensitivity. If closing the meatus reflects the whole of the sound-waves back, the result would be stationary vibrations with twice the primary amplitude—*i. e.*, the intensity at that ear would be increased four times. If, owing to incomplete reflexion or other causes, the increase in intensity were as low as 50 per cent. instead of 400 per cent., it would be a matter for surprise if the increase were not recognizable. We have no quantitative results to argue on, but, *à priori*, one would be inclined to consider it extraordinary if the binaural difference of intensity, produced when the Weber experiment is performed, were not appreciable, if one of the chief effects of closing the meatus is to reflect the waves back again, and to set up stationary vibrations in the ear.

20. If, on the other hand, the physical effect of closing the ear is to make the meatus and its covering into a resonator, the binaural difference of intensity would again, in all probability, be considerable. While, if the tuning-fork sets the whole bony framework of the skull into vibration, as shown diagrammatically in fig. 1 by the whole

Fig. 1.

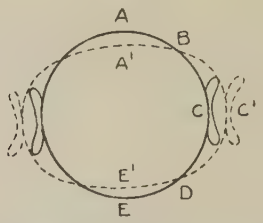


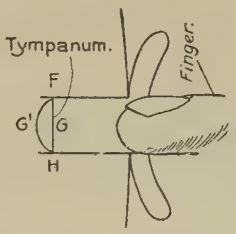
Diagram of possible mode of vibration of the skul.

A, B, C, D, E. One position.
A', B, C', D, E'. Another position.

and the dotted lines, then closing one meatus would perhaps, as suggested by Dr. Hartridge (personal communication), be equivalent to introducing another sound-producing apparatus; for, the tympanum being now prevented from moving with the bones of the head, the ossicles in contact with it are set into vibration relatively to the cochlea with

a frequency equal to that with which the bones of the head are vibrating. This would obviously cause a large increase in the sound at that side (fig. 2).

Fig. 2.



As the bone at C (fig. 1) moves to C′, the air imprisoned by the finger forces the tympanum from the position F, G, H to F, G′, H.

21. So, however the physical effect may operate, we would expect the results of the Weber experiment to be what they are, without it being necessary to assume any great sensitivity on the part of the aural apparatus.

22. I have been unsuccessful in my attempt to repeat the second experiment, Schafer's modification of the Weber experiment, which Myers and Wilson thus describe :—

> "A fork, fixed at some distance from one side of the observer is very gently struck. The observer listens and notes when the dying tone has become quite inaudible. He then inserts an appropriately attuned resonator into the ear which is nearest the fork ; whereupon, of course, the tone is at once softly heard again on that side, as if it came from the resonator. If the meatus of that more distant ear be now closed, the tone becomes at once stronger and its localization approaches the median plane."

23. A change is evident in the phenomenal experience when the finger is inserted in the ear ; but I am unable to discriminate between this change and the change to be observed when the meatus is closed without the resonator being at the other ear. But, if there is bone conduction, which might perhaps be set up by the vibrating resonator inserted in the ear, then closing the other ear would probably, as in Weber's experiment, produce an appreciable increase in the intensity of the sound at that ear, and, in the absence of quantitative measurements, it would be improper to deduce that the ears are extraordinarily sensitive to small binaural differences of intensity caused by bone conduction ; while

to assume that any phenomenal change that may occur is due to an intensity difference does not appear to be warranted.

Conclusions regarding the validity of the assumptions.

24. The result of this examination of the assumptions on which Myers and Wilson base their hypothesis may be briefly summarized as follows :—

(*a*) There is no evidence at present for the assumption that it is impossible to stimulate the end organs of one ear without at the same time stimulating those of the other ear, either by bone conduction or otherwise.

(*b*) Should there be transmission through the head there may be phase retardation.

(*c*) 1. If this phase retardation is between 0° and π, the waves arriving at one internal ear directly through the meatus must be considered as arriving "from opposite directions."

2. If the phase retardation is between π and 2π, it is not necessary to consider that the two sets of waves arrive "from opposite directions."

(*d*) There is no ground for assuming that the ears are exceptionally sensitive to binaural differences of intensity produced by bone conduction.

V. Mathematical Statement of the Myers-Wilson Hypothesis.

25. Now let us consider the argument of the Myers-Wilson hypothesis. It is as follows :—

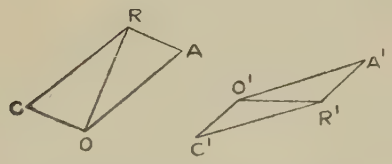
Let OA (fig. 3) represent the physical vibration acting on the ear O, at any given instant, in amplitude and phase, and let O′A′ similarly represent the vibration acting on the ear O′ at the same instant. Then OC ($=\mu \times$ O′A′) will represent the vibration at O at that instant, due to bone conduction from O′, in amplitude and phase, where μ is a constant for the sound, and lies somewhere between the limits 0 and 1. The direction of OC will be determined by the fact that the sound takes a finite time to travel from O′ to O, so that the vibration will be later in phase than that at O′ by an amount which is less than π ; and since the sound is travelling to the ear from the inside, its phase must be reversed. OR will then represent the resultant vibration at O in amplitude and phase. In the same way O′R′ will represent the resultant vibration at O′ in amplitude and phase. It is evident that, if OA leads in phase by an amount less than π, OR

will be greater than O′R′; that is, the sound in the ear O will be louder than that in O′. In consequence of this resulting difference of intensity the sound will be localized on the side O.

26. The theory might with advantage have been stated more fully, for, as Rayleigh * has pointed out, if there is bone conduction the sounds must travel from O to O′, and back to O, and so on till they peter out. Put more generally then, we might say :—

Let OA (fig. 3) represent at any given instant the resultant effect of all the vibrations, due to the sounds which have

Fig. 3.



entered the ear O from the outside, when the stationary condition has been reached at the ear O in amplitude and phase. This will evidently be proportional to the amplitude of the vibration of the external force (P). It will be the sum of the effect of P and of all the previous waves which have travelled from O to O′ and back to O, and which arrive at O at the same instant. There will also be acting on O a force, due to the external force (P′), acting on the ear O′. This force will be the resultant of all the waves which have traversed the various paths from O′ to O an odd number of times. It may be represented, in amplitude and phase, taking account of the assumed reversal of phase, by the line OC.

27. Assuming that the effective force of P on the ear O bears the same relation to the external force P, that the effective force of P′ on the ear O′ bears to the external force P′, and that $OC = \mu \times$ (the effective force of P′ on O′), and $O'C' = \mu \times$ (the effective force of P on O), where μ is a constant ; it follows (1) that the difference of phase between OA and OA″ is equal to the difference of phase between P and P′ ; and (2) that the retardation of the phases of the vibrations received at either ear after traversing the skull an odd number of times will be later than the phases of OA and O′A′ by equal amounts. We may also, in view of the

* Proc. Roy. Soc. lxxxiii. A, pp. 61–64 (1909).

assumed proportionality between the external forces and the *effective* forces, neglect this constant of proportionality and consider P and P′ as the effective forces at the ears.

28. If, now, P is in advance of P′, the phase-difference being ϕ°, and if θ° is the amount by which the vibrations μP and μP′ are behind the vibrations P and P′ respectively, the resulting intensity at O is

$$P^2+\mu^2P'^2-2\mu\,.\,PP'\cos(\phi+\theta), \quad . \quad . \quad . \quad (1)$$

and the resulting intensity at O′ is

$$P'^2+\mu^2P^2-2\mu\,.\,PP'\cos(\phi-\theta). \quad . \quad . \quad . \quad (2)$$

If P = P′, we then have

$$I_0=P^2(1+\mu^2)-2\mu P^2\cos(\phi+\theta), \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$=P^2[(1+\mu^2)-2\mu(\cos\phi\cos\theta-\sin\phi\sin\theta)], \quad . \quad (4)$$

$$I_0'=P^2[(1+\mu^2)-2\mu(\cos\phi\cos\theta+\sin\phi\sin\theta)]. \quad . \quad (5)$$

Subtracting (5) from (4), we have

$$I_0-I_0'=4\mu\,.\,P^2\,.\,\sin\phi\,.\,\sin\theta, \quad . \quad . \quad . \quad . \quad (6)$$

which is Myers and Wilson's value for the intensity differences at the ears, the perception (or, it may be, the unconscious sensing) of which is at the basis of our judgment of direction.

29. This difference of intensity vanishes for $\theta=0^\circ$ or π. It is greatest when $\theta=\pi/2$, so we see that, assuming transmission of sound through the head, the intensity at the ear leading in phase will always be greater than the intensity at the ear which lags in phase, provided the cross-conducted wave suffers a retardation of between 0^c and π, or of $(n\ 2\pi)+\theta$, where θ is between 0° and π, and assuming a phase reversal.

30. If the retardation of the transmitted wave is greater than π but less than 2π, *i. e.* it is equal to $(\pi+\theta)$, it is evident that the same result is obtained for the difference of intensities at the ears, without assuming that the "two (direct and transmitted) sets of waves, at their meeting in one or other ear, arrive from opposite directions"; that is, there is no necessity for the change of sign.

31. In this case, if θ is the whole retardation, the intensities (1) and (2) become

$$P^2+\mu P'^2+2\mu P\,.\,P'\cos(\phi+\theta),$$

and

$$P'^2+\mu P^2+2\mu PP'\cos(\phi-\theta).$$

32. The difference of intensity given by (6) is greatest, for

any given value of θ, when $\phi=\pi/2$. The value then is

$$4 . \mu . P^2 . \sin\theta. \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

33. The greatest possible value of this will result when $\theta=\pi/2$. It will then be

$$4 . \mu . P^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

VI. Calculation of Minimum Value of μ from Experimental Data.

34. Let us now consider the case where there is a difference of physical intensity at the ears, but no phase-difference between the vibrations.

35. If P and P′ are the incoming external stimuli, the resultant intensity at the one ear is evidently, from para. 28 (1),

$$P^2+\mu^2P'^2-2\mu P . P' \cos\theta, \quad . \quad . \quad . \quad . \quad (11)$$

and the intensity at the other is, from (2),

$$P'^2+\mu^2P^2-2\mu P . P' \cos\theta. \quad . \quad . \quad . \quad . \quad (12)$$

The ratio of these intensities is

$$\frac{P^2+\mu^2P'^2-2\mu P . P' \cos\theta}{P'^2-\mu^2P^2-2\mu P . P' \cos\theta} \quad . \quad . \quad . \quad . \quad (13)$$

36. Now, if this ratio of objective intensities produces the same angular localization with reference to the median plane as the ratio of the subjective intensities when there is a difference of phase between the external vibrations, these vibrations being equal in amplitude, then these two intensity ratios can be equated, if we assume that the ear appreciates the two intensity ratios in the same way.

37. This latter ratio, from equations (3) and (5) (para. 28) is

$$\frac{P^2(1+\mu^2)-2\mu P^2 \cos(\phi+\theta)}{P^2(1+\mu^2)-2\mu P^2 \cos(\phi-\theta)} \quad . \quad . \quad . \quad . \quad (14)$$

38. In a previous experiment * I found that the minimum ratio of the intensities of the external vibrations which produced the same angular localization as a phase-difference of $\pi/2$ was 2·50.

39. Substituting these values in (13) and (14) and equating, we get :

$$\frac{2{\cdot}50+\mu^2-2\mu\times 1{\cdot}6\times\cos\theta}{1+\mu^2\times 2{\cdot}50-2\mu\times 1{\cdot}6\times\cos\theta} = \frac{1+\mu^2+2\mu\sin\theta}{1+\mu^2-2\mu\sin\theta} \quad . \quad . \quad . \quad . \quad (15)$$

* Brit. Journ. Psych. xvi. p. 265 (1926).

If θ is greater than π, and the cross-conducted wave is not supposed to undergo a change of phase of π, the equations are :

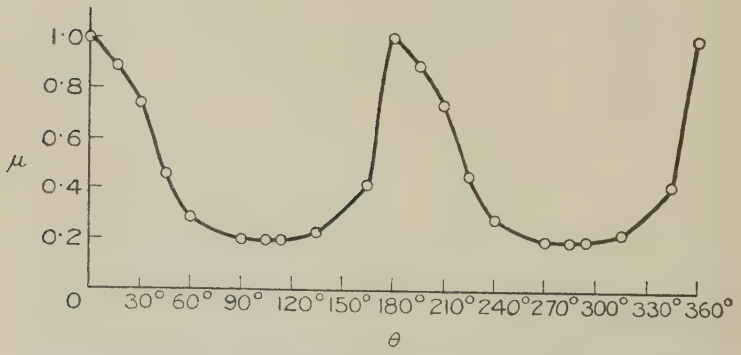
$$\frac{2{\cdot}50+\mu^2+2\mu\times 1{\cdot}6\times\cos\theta}{1+2{\cdot}50\mu^2+2\mu\times 1{\cdot}6\times\cos\theta} = \frac{1+\mu^2-2\mu\sin\theta}{1+\mu^2+2\mu\sin\theta} \quad . \quad . \quad . \quad (16)$$

40. The variation of μ *, as θ increases from 0° to 360°, is shown in Table I. and fig. 4.

Table I.

θ.			μ.
0°	or	180°	1·0
15	or	195	0·89
30	or	210	0·77
45	or	225	0·46
60	or	240	0·29
90	or	270	0·20
105	or	285	0·20
115	or	295	0·20
135	or	315	0·23
165	or	345	0·42

Fig. 4.



The values of μ and θ which satisfy the equations (15) and (16).

μ = proportion of sound which is transmitted through the head from one ear to the other.

θ = phase-retardation of the transmitted wave.

* The method of obtaining the value of μ for any given value of θ is given in the Appendix.

41. The graph shows very clearly that, if the phase-effect is a subjective differential intensity effect, which is produced by the transmission of the sound through the head from one ear to the other, and if this difference of intensity is proportionally the same as that which is required objectively to produce an equal angular displacement of the sound from the median plane when there is no difference of phase between the external vibrations, the proportion of the sound which is transmitted through the head will have a value between ·20 and 1·0, depending on the retardation in phase brought about by the transmission.

42. If the retardation of phase is small, as Myers and Wilson assume, *e. g.* 15°, then $\mu = 0{\cdot}89$. This would mean that, if the right ear were stimulated directly, the amplitude of the vibration transmitted to the left ear would be 89 per cent. of that at the right ear.

43. Under the most favourable conditions, when the phase retardation is about 90° to 120° (or 270° to 300°), the amount of sound conducted through the head is about one-fifth.

44. Now this is *the minimum* value for μ. It is obtained by assuming the most favourable value for the phase-retardation, and using the smallest value (2·50 : 1) for the intensity ratio which would produce the same angular localization as a phase difference of $\pi/2$. For the intensity ratio of 11·8 : 1, the maximum for my observers *, the minimum value of μ, with the most favourable phase-retardation, is ·35. For Stewart's † figure of 33 : 1 for the intensity ratio the minimum value of μ is greater still.

45. It seems very improbable that, if μ has even the smallest value (0·20), my previous experiments ‡, when I was searching for evidence for the direct transmission of sound through the head, could have produced only negative results. Also, if there is transmission of this magnitude, individuals, deaf in one ear, should have little difficulty in hearing with the normal ear sounds, led to the deaf ear: but it is stated § that such individuals cannot hear unless the intensity of the sound is raised to about 10,000 times that required for audition if the sound is led to the good ear directly.

46. This investigation would, therefore, seem to indicate that the Wilson-Myers explanation of the phase effect is not correct.

* Brit. Journ. Psych. xvi. p. 286 (1926).
† Phys. Rev. 2nd ser. xv. p. 425 (1920).
‡ Phil. Mag. July 1926, p. 144.
§ Wegel & Lane, Phys. Rev. xxiii. pp. 266-285 (1924).

VII. Change in the Total Intensity of a Sound with Variations in Relative Phases at the Ears.

(a) *Changes to be expected.*

47. If the ears are being stimulated with sounds of equal objective amplitude, but differing in phase, the effective intensities of the sounds at the ears, assuming transmission of the sound through the head from one ear to the other, are given by (4) and (5), para. 28. These are:

$$P^2 [(1+\mu^2) - 2\mu (\cos\phi \cos\theta - \sin\phi \sin\theta)]$$

and $$P^2 [(1+\mu^2) - 2\mu (\cos\phi \cos\theta + \sin\phi \sin\theta)].$$

The total intensity of the sound is therefore

$$2P^2 [(1+\mu^2) - 2\mu \cos\phi . \cos\theta]. \quad . \quad . \quad (17)$$

48. For any given individual and a tone of given pitch, μ and θ will be constant. We therefore have that the total intensity will vary as the relative phases of the external vibrations vary. It will be a maximum when

$$2\mu \cos\phi \cos\theta \text{ is a minimum}; \quad . \quad . \quad . \quad . \quad (18)$$

and a minimum when

$$2\mu \cos\phi \cos\theta \text{ is a maximum.} \quad . \quad . \quad . \quad . \quad (19)$$

Since μ and θ are constant,

$2\mu \cos\phi \cos\theta$ will be a minimum when

$\cos\phi$ is a minimum.

The smallest value of $\cos\phi$ is -1 when $\phi = 180°$;

The greatest value of $\cos\phi$ is $+1$ when $\phi = 0°$.

49. So we see that the total intensity of the sound is, according to the Myers-Wilson hypothesis, a maximum when the difference between the phases of the external vibrations is 180°: it is a minimum when the vibrations are in phase.

50. This same relation holds, if the phase-retardation of the transmitted sound (θ) is between π and 2π, if no change of phase is postulated.

51. For other cases (θ less than π, and no change of phase; or θ between π and 2π and a change of phase) the total intensity will be a maximum when the external vibrations are in phase and a minimum when their phases differ by π. But if the maxima and minima vary in this way, the experiment furnishes evidence which is a direct contradiction of the Myers-Wilson hypothesis.

(b) *Changes observed by previous experimenters.*

52. A certain amount of work has already been done on the variation in the intensity of binaurally heard sounds with change in the relative phases at the ears; but, as I shall show, the results do not agree.

53. The variation of relative phase has usually been obtained by leading sound waves from two slightly mistuned forks, or other sources of sound, to the ears separately. Binaural beats then occur, and the various phenomena connected with these beats can be observed as the relative phases at the ears vary from 0° to π and back again to 0°.

54. *Thompson*, 1877.—Thompson * was one of the first to remark on variations of intensity so observed. With slow beats, less than two per second, he says :—

> "There was no very decided weakening of the intensity of the sound comparable to the 'silences' ordinarily observed between the 'beats,' the two tones seeming to be going on, but with a difference hardly definable in precise terms. When complete difference of phase was momentarily attained, there seemed to be a slight increase in the intensity of the sound, and the octave note (which, it will be remembered, is not amongst the upper partials of the fork) was faintly heard."

So, though he did not find any "very decided weakening," there still "seemed to be a slight increase in the intensity of sound" when there was a difference of phase of π. A result which supports the Myers-Wilson hypothesis.

55. *Rostosky*, 1902.—Rostosky † noted intensity variations in binaural beats in 1902; but he found the maximum intensity was when the sounds were in phase, and that, when the beats were slower than one in two to five seconds, other maxima appeared just before and just after the opposition of phase. These observations are antagonistic to the Myers-Wilson hypothesis. The maxima and minima are reversed, while secondary maxima occur!

56. *More & Fry*, 1907.—Five years later More and Fry ‡ paid attention

> "to the question whether difference in phase produced a change in the intensity of the combined tones. . . . . Not one of [14] observers could detect any alteration in the loudness of the sounds when the relative phases were varied."

* Phil. Mag. (5) iv. pp. 274–276 (1877).
† Philos. Stud. xix. pp. 557–598 (1902).
‡ Phil. Mag. [6] xiii. pp. 452–457 (1907).

These experimenters, I would remark, used apparatus similar to that employed later by Myers and Wilson. They obtained their difference of phase by varying the lengths of the pathways by which the sounds were led from a single source to the ears. They did not study the phenomena of binaural beats.

57. *Stewart*, 1917.—In 1917 Stewart * published the result of an investigation he made into the maxima and minima to be observed with binaural beats, with special reference to Rostosky's experiments. He remarks * :—

> "One [maximum intensity] occurred at 0° difference of phase, one at $180°-\delta$ and one at $180°+\delta$, δ being less than 45°. The earlier of the additional maxima at $180°-\delta$ phase difference coincided with the localization in the ear near the higher frequency, and the latter with the localization in the other ear. . . . . The significant fact is that the 0° maximum was always present, whereas the secondary ones required a beat period exceeding at least a second in order to become clearly evident. . . . . The localization in the ears as described seemed to depend upon the perception of the secondary maxima."

We see, then, that his observations agree with those of Rostosky, but that they disagree with the Myers-Wilson hypothesis.

58. *Banister*, 1925.—My own results, previous to the investigation about to be described—side remarks made by observers in other experiments—had shown equal diversity. Only once † had an observer specially attended to intensity differences. I was then determining the binaural intensity ratio which would produce the same angular localization of a tone as a phase-difference of $\pi/2$. This observer correctly picked out the "phase-effect," differentiating it from the intensity effect, because with the former he could not appreciate any change in the loudness of the sound.

59. We see, then, that there is a difference of opinion, first of all whether a change in the relative phases of the vibrations at the ears causes any change in the loudness of the sound or not; secondly, whether the maximum, if there is one, is when the vibrations are "in phase" or when the phase-difference is 180°.

* Psych. Monogr. xxv. pp. 31–46 (1917–18); Phys. Rev. ix. pp. 502–528 (1917).

† Brit. Journ. Psych. xvi. p. 288 (1926).

(c) *Disadvantages of the "Binaural Beat" method of investigation.*

60. Now, though a study of variations in loudness due to phase changes is experimentally most easily made by listening to binaural beats, phenomenally such a method of investigation is fraught with difficulty. The sound is moving about from side to side all the time, and the way in which it moves is different for different people—some (*e. g.* Stewart) appear to hear the sound outside the head in front for a part of the cycle and inside the head for the rest; others hear the sound behind instead of in front; others only hear the sound inside the head; with some the sound travels in a horizontal plane; with others the same sound physically moves in a plane, making an angle of perhaps 60° with the horizontal. Again, with some observers the pitch of the sound varies with its position, while, more important still, the apparent distance of the sound varies from point to point. Another most important attribute, very distinct from loudness, but yet one which may easily be confused with loudness, is volume; and volume again varies with position, though what the relation between volume and phase difference at the ears is has not yet been settled. The observations so far available—*e. g.* Wilson and Myers *, Peterson †, Halverson ‡—are not sufficient for any generalizations to be made. Now it is evident that one and all of these factors may enter into our judgment of "loudness"; so that it would seem desirable to eliminate them, as far as is possible, by using sounds which are not continually changing in position.

61. Another very serious objection to the binaural beat method of study is that no controls are possible, and the same error, should there be one, will creep in again and again, and may perhaps be accentuated by use.

(d) *Necessity of further investigation.*

62. It therefore seemed important that an investigation should be made into the variations in loudness produced by changing the relative phases of the vibrations of the sound waves at the ears, the amplitudes of the vibrations being kept constant.

* Brit. Journ. Psych. ii. p. 369 (1908).
† Phys. Rev. xxiii. pp. 333–351 (1916).
‡ Psych. Monogr. xxxi. pp. 7–29 (1922); Amer. Journ. Psych. xxxiii. p. 179 (1922).

(e) *Experimental determination of the change in intensity.*

(i.) *Apparatus.*

63. The apparatus was that used in previous experiments *, and is shown diagrammatically in fig. 5.

Fig. 5.

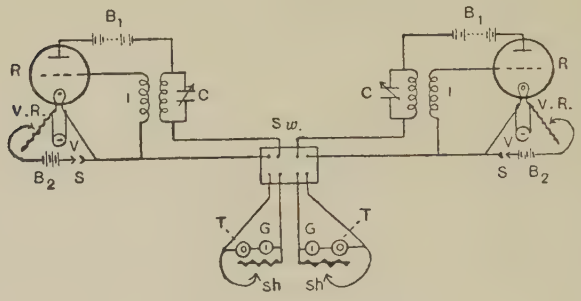


Diagram of Apparatus.

B_1. High-Potential Battery (54 volts.). B_2. Accumulator (6 volts). C. Variable Condenser. G. Milliammeter. I. Inductances. R. Valve. S. Switch. *sh.* Shunt. T. Telephone. V. Voltmeter. V.R. Variable Resistance. *Sw.* 4-way Switch.

(ii.) *Experimental Technique.*

64. The observer, with head-phones on, sat in the sound-proof room ; the experimenter in the annexe. Communication was, as before, by microphone from Observer to Experimenter and by speaking-tube from Experimenter to Observer. When ready, the observer said " Ready ! ", and the sounds, in phase, were switched on. The sound was then centred and switched off. After a short interval the sounds were switched on to verify that the sound was still in the median plane ; if it were not, adjustments were made. This was repeated, if necessary, till the observer reported that the sound was in the centre. The current passing through the telephones was then noted. (This current is, as I have already shown †, proportional to the amplitude of vibration of the telephone diaphragm.) The experiment then began. The experimenter switched on the sounds. The observer listened,

* Brit. Journ. Psych xv. pp. 280–307 (1925); xvi. pp. 265–292; Phil. Mag. July 1926, p. 144.

† Brit. Journ. Psych. xvi. p. 281 (1926).

satisfied himself that he had the sound properly under observation, signalled to that effect by gently touching the microphone, and listened to see if he detected any change in loudness. The experimenter meanwhile made a change in phase of π, or a change of intensity—either increasing or decreasing the intensity—or else he made no change at all. The sounds were continued for about four seconds, and then switched off. The observer wrote down his observation on a specially prepared form, with separate columns for Louder, Equal, and Softer, and remarked on any matter of interest. The experimenter also noted down what change he had made, re-adjusted the apparatus to its initial condition, and waited for the "Ready!" from the observer, when the next observation was taken. Since the observer had to judge changes in loudness only, the sounds were not centred for each observation. Variations in the position of the sound were sometimes remarked on; but, though of interest, the observations made are too scattered to justify discussion here. The sound was centred before the first and the eleventh observations only—*i. e.*, when the telephones were first put on and when they were changed round. The sound used was an impure tone of about 220 d.v./sec.

65. Twenty observations were taken at each sitting, which usually lasted for about half-an-hour.

66. Four observers, two men and two women, took part in the experiment. Three of them, A, B, and F, had observed for me previously. The fourth, (G), a man, was new. The observers were not equally able to give me of their time, so the number of observations obtained from them is not constant.

(iii.) *Reports of Observers.*

67. The reports are summarized in Table II., which shows, for example, that the experimenter decreased the amplitude of the vibration at one ear to between 81 per cent. and 90 per cent. of its initial value eighteen times for observer A, who judged that the sound became louder three times, softer eleven times, while she detected no change in loudness four times. The experimenter made "no change," either of phase or of intensity, nineteen times for observer B, who reported that there was no change in loudness on twelve of these occasions, but that, on the other seven occasions, the sound appeared to become softer.

Table II.

Change made by Experimenter. / Observer.	Initial amplitude of the vibration at one side: decreased to between these percentage limits.												No change.		Phase-change 0° to π.	
	0–70		71–80		81–90		91–100		101–110		111–120		121–130		131–140		141–150		151–					
	L	E	S	L	E	S	L	E	S	L	E	S	L	E	S	L	E	S	L	E	S	L	E	S	L	E	S	L	E	S	L	E	S	L	E	S	L	E	S	L	E	S
A	–	1	4	2	2	7	3	4	11	–	1	1	1	1	1	7	5	–	11	3	–	–	–	–	1	–	–	2	–	–	5	21	4	7	36	3
B	–	–	3	–	2	1	4	1	3	–	1	–	–	–	–	8	3	–	2	1	–	2	1	–	–	–	–	–	–	–	7	12	–	12	9	1
F	–	1	1	–	–	2	1	4	3	–	1	1	–	2	1	4	2	–	4	–	–	–	–	–	1	–	–	1	–	–	1	10	2	10	11	3
G	1	–	1	1	8	1	8	7	–	–	–	–	2	–	–	5	3	–	9	–	–	1	–	–	1	–	–	2	–	–	13	17	–	24	9	–

Table showing the number of times each observer judged that the change made by the experimenter caused the total sound to appear to grow louder (L), to grow softer (S), or to remain of constant loudness (E).

68. It will be noticed that every observer reported an increase of loudness more often than a decrease when the relative phases at the ears were varied from 0° to π, and that two (B & G) showed a very marked tendency to judge that the sound had become louder. This is, *prima facie*, evidence for the Myers-Wilson hypothesis.

69. But let us examine the whole data more fully, beginning with F. F clearly differentiated the "No change." On three out of thirteen such observations he recorded changes of loudness—once an increase and twice a decrease. He, also, could discriminate and judge correctly when the amplitude of the vibration to one side was increased to 111 per cent. or more of the initial amplitude, or when it was decreased to 90 per cent or less. Out of twenty-four observations, when the phase was changed from 0° to π, he reported an increase in loudness ten times, "No change" eleven times, and a decrease three times. This observer had four sittings. At the first, his report for the phase-change was 5 louder ; 3 equal ; nil softer.

At the second, he reported	4	„	; 3	„	; 1 softer.
At the third, „	nil	„	; 1	„	; 2	„
At the fourth, „	1	„	; 4	„	; nil	„

He made no introspective remarks of interest. But the fact that at his third and fourth sittings he reported one louder, five equal, and two softer would seem to point to the possibility of his having learned with practice to discriminate variations of loudness from variations in other ways.

70. (A) discriminated the "No change" fairly successfully, but for the phase-change reported more increases than decreases in loudness. She also could, obviously, tell when the amplitude of the vibration at one side was increased, or decreased, by 10 per cent.

71. A gave me eight sittings. Her reports, when the relative phases were changed from 0° to π, were :—

Louder.	Equal.	Softer.	Remarks by Observer.
2	4	0	x Equal or softer.
2	6	0	* Equal or louder.
2	5	1	
–	2	1x	
1*	4	1x	
–	5	–	
–	5	–	
–	5	–	
7	36	3	

72. We see that, after her first three sittings, she reported changes of loudness only three times out of twenty-four observations, and, on each of these three occasions (of which only one was a judgment of increase), she queried the change.

73. This observer's remarks are interesting. The first day she reported much difficulty in forming a judgment of loudness when listening to the phase-change, but none when the phase did not change. She ascribed this to the movement which occurred. Her remarks for the two occasions on which she reported an increase were "Large change in position—very muddling." "Very difficult because of change in position." But before the end she began to differentiate, and she remarked that what she at first thought was an increase in loudness was really some change or other in what she called "quality"—some change she found it difficult to describe. Thereafter this uncertainty gradually gave way to certainty that there was no variation in loudness, but some other change, due somehow or other to the change in the position of the sound, which change in position she later decided was a movement from one point in the median plane to some other point in the median plane. When the sound was at the second position in the median plane (phase-difference π), she described it as "a curiously exciting noise. It is very thrilling. It gives me the impression of going up and perhaps becoming clearer."

74. (A) therefore, if the first sittings are considered, as they reasonably may, to be preliminary practice sittings, definitely could not distinguish any change in the intensity of the sounds when the relative phases at the ears were changed from 0° to π, though she could discriminate a change in the amplitude of the vibration at one side of 10 per cent.—which is a change of not more than 10·5 per cent. in the total physical intensity of the sounds acting on her ears.

75. But (B) and (G) are different. They both, on the average, judged that the sounds had become louder when the relative phases were changed from 0° to π; and also they judged that the sound became louder even when no change whatever was made. (B) came only four times, whilst (G) came six times. Their judgments on each of these occasions were :—

Observer.	No change made.			Relative phases changed from 0° to π.		
	L	E	S	L	E	S
(B)	3	–	–	1	4	1
	3	4	–	2	1	–
	1	3	–	5	2	–
	–	5	–	4	2	–
	7	12	0	12	9	1
(G)	6	1	–	2	1	–
	2	2	–	5	–	–
	2	3	–	4	2	–
	1	4	–	4	2	–
	1	4	–	4	2	–
	1	3	–	5	2	–
	13	17	0	24	9	0

L = Louder. E = No change. S = Softer.

(G), it will be noticed, judged at his first sitting that the sound went louder six times out of the seven times no change was made; the next sitting he judged more correctly, and, though there was still a tendency to judge that the loudness was increased when no change was made in the intensity, he discriminated the "No change" observations with reasonable accuracy at his fourth and subsequent sittings. He, however, still continued, in no uncertain manner, to judge that there was an increase in loudness when the relative phases were varied from 0° to π. (B)'s results show a very similar tendency.

76. These two observers are also alike in another respect. They judge, as a reference to Table II. will show, that the sound *increased in loudness* when the *physical intensity decreased*, provided the decrease was not too great. It will be seen that, when the amplitude to one side was decreased from 81–90 per cent., (B)'s judgments for 8 observations were: 4 louder, 1 equal, and 3 softer; while (G) judged 15 observations to be 8 louder and 7 equal.

77. In spite of these peculiarities, it might be argued that the evidence of these two is in favour of the Myers-Wilson hypothesis. It is not a sufficient answer to state that the

observers were judging a change in some other attribute of situation as an increase of loudness. The obvious course was to try the same experiment again, but this time to vary the phases the opposite way, from π to 0°. Since the change from 0° to π produced an increase in loudness, a change from π to 0° should cause a decrease in loudness. Unfortunately, one observer left Cambridge temporarily, while the other become ill, so the experiment could not be performed till six weeks later, when observer (A) also gave me two more sittings. The observations then obtained when "No change" was made, and when the relative phases were varied from π to 0°, were:—

Observer.	No change made.			Relative phases changed from π–0.		
	L	E	S	L	E	S
B (2 sittings)	3	8	0	10	3	0
G (3 sittings)	5	9	1	10	10	0
A (2 sittings)	0	10	0	1	14	0

L = Louder. E = No change. S = Softer.

78. It will be seen that (A)'s report agrees with her previous ones. She reported a change of "some description," but not of loudness when the relative phases were changed from π to 0°; while (B) and (G) showed the same tendency to report an increase of loudness when "No change" was made, and, instead of the phase-change producing a *decrease* in intensity, an *increase* was reported. It therefore, I think, appears evident that, in judging the sound to have become louder, these two observers were not discriminating the loudness from the other factors in the situation.

79. It would seem that this is the true explanation of the observations of Thompson, Rostosky, and Stewart. In judging variations in loudness, they probably did not discriminate—their experimental method made it almost

impossible—between variations in loudness and variations in the other attributes of the sounds they used. Also their experiments lacked control, as I have pointed out in para. 61.

(iv.) *Conclusion.*

80. The conclusion to which this experiment forces us is, therefore, that, if tones of the same frequency are led separately to each ear, there is no appreciable difference in the loudness of the resulting sound whatever the relative phases of the vibrations may be, provided the amplitudes are kept constant; while there is evidence that a change of 10 per cent. in total intensity is discernible *.

VIII. Summary of the Results.

81. Let us now briefly summarize the results arrived at in this and other papers †, so far as they bear on the hypothesis that the "phase-effect" is to be explained as an "intensity effect" brought about by the transmission of sound energy from one ear to the other through the head.

82. (1) The evidence for the first assumption made by Myers and Wilson, that "the sound entering one ear is transmitted through the bones of the head to the opposite ear," has been examined †. It has been shown that the experimental evidence adduced in support of the assumption will not stand critical examination. The most refined experimental methods, so far used, have failed to demonstrate that there is any transmission of sounds of ordinary intensities from one ear to the other, either by bone conduction or by any other means, in the living head.

83. (2) The second assumption, "that the retardation in phase due to such internal conduction is small," may be accepted. Unless there is some phase-difference, the transmission of the sound could not produce any binaural intensity difference. At the same time the magnitude of this assumed phase-retardation is immaterial to the general argument.

84. (3) The third assumption, "that the two sets of waves thus received at each ear directly and by bone conduction, meet coming from opposite directions," was made to account for the facts. It is necessary to assume this change of phase if the phase-retardation (assumption 2) is small. If the phase-retardation is between π and 2π, this change of phase need

* This 10 per-cent. limen must not be considered as anything more than indicating that my observers could appreciate this variation in intensity with sounds of the loudness used. But it agrees with the value found by Knudson (Phys. Rev. xxi. pp. 84–102, 1923).

† Brit. Journ. Psych. xvi. p. 265 (1926). Phil. Mag. July 1926, p. 144.

not be assumed. There is a difference of opinion among physiologists as to the legitimacy of the assumption, but our knowledge of the whole mechanism of the transmission of sound through the head, if it takes place, is so nebulous that the assumption cannot profitably be criticized.

85. (4) Binaural difference tones cannot be heard, though binaural beats can. If the latter are due to interference at the end organs, due to transmission of the sound through the head, it is difficult to understand why binaural difference tones cannot be obtained *.

86. (5) Assuming that the Myers-Wilson hypothesis is correct, and that the phase-effect is on analysis an intensity effect, experiments were performed † to determine what differences of objective physical intensity at the ears, when the vibrations were in phase, would produce the same angular localization of the sound as a phase-difference of $\pi/2$ when the intensities of the sounds remained equal.

87. Two methods were employed: (*a*) the "Method of Production," the relative intensities being varied till the sound appeared to occupy the same angular position, with reference to the median plane, as it occupied when the relative phases only were changed; and (*b*) the "Method of Presentation," the observer reporting whether a given binaural intensity-difference produced a greater, equal, or lesser angular localization of sound with reference to the median plane when compared with the deviation produced by the phase-difference.

88. The two methods show a remarkable agreement for individual observers; but there are great differences between the various observers. The least binaural ratio of intensity required to produce the same angular localization as was caused by a difference ‡ of phase of $\pi/2$ was 2·5 : 1; the greatest was 11·8 : 1.

89. (6) If a binaural ratio of intensity of 2·5 : 1 could result from the transmission of sound through the head, the minimum value for μ (the ratio of the subjective amplitudes of the vibrations at the ears when a sound is led to one ear) is ·20—the phase-retardation would then be about 90° to 120°. For a binaural intensity ratio of 11·80 : 1 the minimum value of μ is ·35.

90. It is incredible that such large proportional amounts of energy could be transmitted and escape detection. (This paper, paras. 34–46.)

* Phil. Mag. July 1926, p. 144.
† Brit. Journ. Psych. xvi. p. 265 (1926).
‡ Brit. Journ. Psych. xvi. p. 286 (1926).

91. (7) If the "phase-effect" is due to transmission through the head, the total sound heard should vary in loudness as the relative phases of the vibrations at the ears vary. The total sound will, according to the Myers-Wilson statement of the hypothesis, be loudest when the vibrations differ in phase by π, and quietest when there is no difference in phase. (If the phase-retardation due to the transmission lies between π and 2π, the opposite effect will occur.) Carefully controlled experiments produced no evidence for this variation in loudness. At the same time, a difference of total intensity of 10 per cent. was easily appreciated. (This paper, paras. 47–80.)

92. (8) According to the Myers-Wilson hypothesis, the phenomenal effects of varying the bilateral intensities of the sounds at the two ears should be independent of the relative binaural phases. This is not borne out by experiment. The observed facts agree with the hypothesis that the phase-effect is not an intensity effect *.

IX. Conclusion.

93. We see, then, that the Myers-Wilson hypothesis has in no single instance been supported by experiment. The conclusion is that any hypothesis is wrong which seeks to explain the facts, of sound-localization by binaural phase-differences, on the assumption that there is transmission of sound from one ear to the other through the head, and that this transmission causes the actual intensity of the sound at the ear which leads in phase to be greater than the intensity at the ear which lags in phase.

Appendix.

Method for determining the graph for μ as a function of θ from equation (15), para. 39 :

$$\frac{2{\cdot}50+\mu^2-3{\cdot}2\mu\cos\theta}{1+2{\cdot}50\mu^2-3{\cdot}2\mu\cos\theta}=\frac{1+\mu^2+2\mu\sin\theta}{1+\mu^2-2\mu\sin\theta}.$$

Plot the curves $$y_1=\frac{2{\cdot}50+\mu^2-3{\cdot}2\mu\cos\theta}{1+2{\cdot}50\mu^2-3{\cdot}2\mu\cos\theta}$$

and $$y_2=\frac{1+\mu^2-2\mu\sin\theta}{1+\mu^2-2\mu\sin\theta}$$

between the limits $\mu=0$ and $\mu=1$, for various values of θ.

The point of intersection of the curves gives, evidently, the value of μ which satisfies equation (15) for the specific values of θ taken

* Brit. Journ. Psych. xvi. p. 265 (1926).

For example :

Let us find the value of μ if θ, the phase-retardation in passing through the head from one ear to the other, is 60°.

If $\theta = 60°$, $\sin\theta = \cdot 87$, $\cos\theta = \cdot 5$, so the equations for y_1 and y_2 may be written

$$y_1 = \frac{2\cdot 50 + \mu^2 - 1\cdot 6\mu}{1 + 2\cdot 50\mu^2 - 1\cdot 6\mu},$$

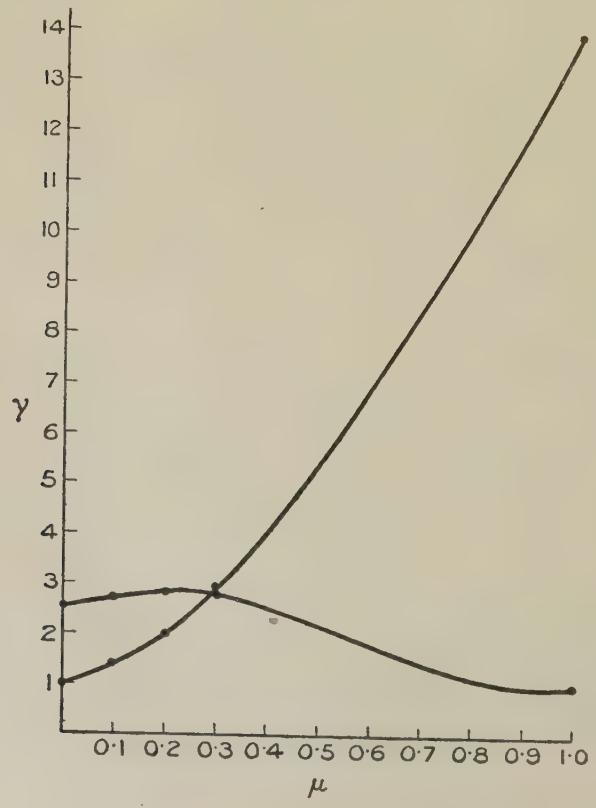
$$y_2 = \frac{1 + \mu^2 + 1\cdot 74\mu}{1 + \mu^2 - 1\cdot 74\mu}.$$

Evaluating y_1 and y_2 for various values of μ between 0 and 1, we get

μ.	y_1.	y_2.
0	2·50	1
·1	2·7	1·4
·2	2·85	2·0
·3	2·83	2·9
1·0	1	14·4

Plotting these values of y_1 and y_2, we obtain the curves of fig. 6.

Fig. 6.



From which we get, by inspection, the value of μ as 0·29 when $\theta = 60°$.

In a similar way we find the following pairs of values, which on plotting give the curve of fig. 4, para. 40 :—

θ	0°	15°	30°	45°	60°	90°
μ	1	0·89	0·77	0·46	0·29	0·20

θ	105°	115°	135°	165°	180°
μ	0·20	0·20	0·23	0·42	1·0

XXXIV. *The Elasticity Coefficients and the Thermodynamic Integration Factor for the Solid State. By* A. Press, *Rockefeller Foundation Visiting Professor of Physics, Chulalongkorn University, Bangkok, Siam* *.

The Generalized Thermodynamic Equation of State.

THE work of Grüneisen and Ratnowsky, mentioned in the text of Andrews's article on "The Relation between Young's Modulus and the Temperature" (see Phil. Mag. October 1925, p. 667), led to the questioned conclusion "that $\frac{V\beta}{k_T}$ should be the same function of the corresponding temperature for all substances...." Here k_T is the isothermal compressibility, V the atomic volume, and β the coefficient of cubical expansion. The above formula, be it noted, was derived by Ratnowsky by applying the quantum theory to Grüneisen's work after the Debye manner. In checking up the above formula, it was found that the metals Fe, Ni, Zn; Ag, Sn; Au, Pt, Pb, for example, grouped together rather according to the same row of the periodic table than according to the same column, which result was quite unexpected. It will be shown herewith, however, on theoretical grounds that a density factor d should have

* Communicated by Prof. I. J. Schwatt, Ph.D.

occurred in the formula to justify the observed row grouping of the elements.

It is also to be borne in mind that if at points far removed from the actual change of state the ratio $\frac{\beta}{k_T}$ can be made to conform to a modified Grüneisen-Ratnowsky type of formula, for a proper generalized understanding of all the thermodynamic factors to appear, one and the same covering expression for such ratio should obtain for the change of state itself. That is to say, the one general formula should lead to the expression $\frac{\beta}{k_T} = \frac{\lambda}{t}$, where λ is now the internal latent heat of the body. (See Edser, Fourth Report on Colloid Chemistry, Brit. Assoc. Adv. Sci. 1922.) It will be shown that the generalized thermodynamic treatment herewith satisfies the above two conditions. Indeed, it also leads to the further Grüneisen condition that the specific heat at sufficiently low temperatures is proportional to the thermal coefficient of expansion divided by the compressibility. In accordance with Debye, it is known that the compressibility should also vary little with the temperature.

The starting-point is therefore to be made with the energy equation

$$dQ = \frac{\partial U}{\partial t} \cdot dt + \left(\frac{\partial U}{\partial v} + p\right) dv.$$

Instead, then, of employing the more usual integrating factor $\mu = 1/t$, which, in fact, mathematically at least, limits the solution considerably, a more general type of integrating function

$$\mu = f(t, v)$$

will be taken with the understanding that the precise form of μ is to be deduced theoretically as a consequence of experimental fact. Thus applying the condition for a complete differential, we have that

$$p + \frac{\partial U}{\partial v} + \frac{\mu}{\frac{\partial \mu}{\partial t}} \cdot \frac{\partial v}{\partial t} = \frac{\partial U}{\partial t} \cdot \frac{\frac{\partial \mu}{\partial v}}{\frac{\partial \mu}{\partial t}}.$$

The above is to be regarded as a General Equation of State applying to all bodies, solid, liquid, or gaseous. It is the right-hand term that would be missing with the usual limiting mathematical treatment.

The Elasticity Function β/k_T.

Since by definition we have that

$$k_T = C = -\frac{1}{v}\cdot\frac{\partial v}{\partial p} = \text{compressibility constant},$$

$$\beta = \frac{1}{v}\cdot\frac{\partial v}{\partial t} = \text{expansibility coefficient},$$

and therefore $$\frac{\beta}{k_T} = \frac{\partial p}{\partial t}.$$

Substituting the latter in the general equation of state, it follows that

$$\frac{\beta}{k_T} = \frac{\dfrac{\partial \mu}{\partial v}}{\mu}\cdot\frac{\partial U}{\partial t} - \frac{1}{\mu}\cdot\frac{\partial \mu}{\partial t}\cdot\left(1+\frac{p}{\dfrac{\partial U}{\partial v}}\right)\cdot\frac{\partial U}{\partial v}.$$

The quantity $p\Big/\dfrac{\partial U}{\partial v}$ represents the ratio of external to internal work performed at constant temperature.

From the above it is seen at once that two important limiting conditions are indicated. The one is when the body is about to change its state (as at fusion, or boiling, Edser-Lewis condition), and the other is when the body is far removed from the latter critical condition. Supplemental, therefore, to the work of Grüneisen and Ratnowsky, it is particularly significant that a general formula can be derived thermodynamically to cover both types of conditions at one and the same time.

The Grüneisen-Ratnowsky Type of Function.

At temperatures sufficiently far removed from the change of state where the function $\dfrac{\partial U}{\partial t}$ is naturally predominant over $\dfrac{\partial U}{\partial v}$ or the effect of the p-term, we have the limiting condition

$$\left.\frac{\beta}{k_T}\right|_0 \equiv \frac{1}{\mu}\cdot\frac{\partial \mu}{\partial v}\ \frac{\partial U}{\partial t}.$$

If, then, with Andrews, we write

V = atomic volume,

d = density,

it follows, on assuming that Dulong and Petit's law prevails, that

$$\frac{\partial U}{\partial t} \equiv \frac{6.6}{Vd},$$

so that on substitution, we have

$$\frac{\beta}{k_T}\Big|_0 \equiv \frac{6.6}{Vd} \cdot \frac{1}{\mu} \cdot \frac{\partial \mu}{\partial v}.$$

The latter will also lead to the Grüneisen specific heat condition

$$\frac{\beta}{k_T}\Big|_0 \equiv A \cdot \frac{\partial U}{\partial t},$$

provided it can be proved that

$$\frac{1}{\mu} \cdot \frac{\partial \mu}{\partial v} = \text{constant},$$

and not zero as hitherto assumed. It is precisely the former condition that is satisfied by the needed grouping of the metals according to rows, as Andrews found to be the case. The metals Fe, Ni, Zn; Ag, Sn; Au, Pt, Pb, are naturally grouped according to atomic weight, so that there was experimental justification for the statement of Andrews (see *l. c.* p. 667, footnote) "that to each of the above groups the relation $\left[\frac{V\beta}{k_T} = \psi(t)\right]$ applied separately, as an approximation which extends up to half the absolute temperature of fusion." For the exact equation see further.

The Thermodynamic Integration Factor for the Solid State.

Integrating the differential equation of condition above, we have that

$$\mu = \psi(t) \cdot \epsilon^{Av}$$

so that the Grüneisen-Ratnowsky type of formula should really read

$$\frac{V\beta}{k_T} = \frac{6.6A}{d} \cdot \psi(t),$$

and all "logical difficulty" is avoided. It is significant that the above development has not had to depend on the quantum theory and is rather supplemental than in contradiction to it.

For the solid state, therefore, we have the equation of state

$$p + \frac{\partial U}{\partial v} + \frac{\frac{\partial p}{\partial t}}{\frac{d}{dt}\lg\psi} = \frac{A}{\frac{d}{dt}\lg\psi}\,\frac{\partial U}{\partial t},$$

where ψ is a function of t only.

The Edser-Lewis Latent Heat Formula.

Turning now to conditions about the change of state where the term $\frac{\partial U}{\partial v}$ predominates over $\frac{\partial U}{\partial t}$, the elasticity function becomes

$$\frac{\beta}{k_T}\Big|_C \equiv -\frac{1}{\mu}\cdot\frac{\partial \mu}{\partial t}\left(1 + \frac{p}{\frac{\partial U}{\partial t}}\right)\cdot\frac{\partial U}{\partial v}.$$

Thus, with Edser, writing λ for the internal heat per unit volume, it is found that practically

$$\frac{\beta}{k_T}\Big|_C \equiv -\lambda\cdot\frac{1}{\mu}\cdot\frac{\partial \mu}{\partial t}.$$

In the case of gases for which $\frac{1}{\mu}\frac{\partial \mu}{\partial t} = \frac{1}{t}$, we at once arrive at the result of Edser-Lewis. More generally, if we assume

$$-\frac{1}{\mu}\cdot\frac{\partial \mu}{\partial t} = \phi(v)\,.\,F(t),$$

on integration we obtain

$$-\lg\mu = \phi(v)\,.\int F t\,.\,dt = \phi(v)\,.\,\lg f(t),$$
$$\mu\,.f(t) = \phi(v).$$

Clearly for the state near the point of ebullition a more general type of function would be

$$\mu = at^m\,.\,\phi(v),$$

which on substitution would give

$$\frac{\beta}{k_T}\Big|_C \equiv \frac{m\lambda}{t}.$$

The Integrating Factor and the Question of Phase.

According to the above analysis the elasticity function $\frac{\beta}{k_T}$ was shown to consist of two parts, of which the one depended on $\frac{\partial U}{\partial t}$ and the second on $\frac{\partial U}{\partial v}$ primarily. Yet according to either limitation, μ consisted of two factors, $\psi(t)$ and $\phi(v)$. If then, for generality, we write as follows:

$$\mu = \psi(t) \, . \, \phi(v),$$

it is quite clear that the precise form of μ as an integrating factor of the thermodynamic energy equation depends firstly upon the considered phase of the substance, and secondly on the conditions prevailing both at the change of state and at points far removed from the change of state. Naturally, for the case of a perfect gas, $\frac{\partial U}{\partial v} = 0$, and therefore $\phi(v)$ would not be present. However, for actual gases near their change of state (very low temperatures), the latent heat condition involving $\frac{\partial U}{\partial v}$ is being approached, so that the more general integrating factor μ as above given ought to be used. This condition should have material influence on the specific heat values as a function of the temperature, and can be used to explain much of Dr. Giacomini's findings recorded in the Phil. Mag. for July 1925, p. 154.

Dec. 1, 1925.

XXXV. *Eddying Flow from Annular Nozzles* *. *By* E. Tyler, *M.Sc.*, *and* E. G Richardson, *B.A.*, *M.Sc.*, *Ph.D.* (*University College, London*) †.

IN 1922 a paper ‡ appeared by Krüger and Marschner on the tones given out by fluid passing through a ring-shaped nozzle, formed by the space between the mouth of a cylindrical tube and a disk concentric with the tube and flush with the mouth. It was thought by the present authors that the system of embryo vortex-rings formed in the issuing

* This work was begun in 1923. The early results and deductions formed part of a Ph.D. Thesis at the Univ. of London, Jan. 1925.

† Communicated by the Authors.

‡ Krüger & Marschner, *Ann. der Phys.* lxvii. p. 581 (1922).

fluid should be mainly governed by the disk, considered as an obstacle in the stream, and that the frequency of production, n, of vortices should be related to the velocity, V, of the stream by the relation: V/nD = constant, D being the diameter of the disk. This relation is that found by Strouhal* for a cylinder in a stream, so that the tones produced would be, in fact, the Æolian Tones of a circular disk, modified possibly by the proximity of the outer tube of the nozzle—the type of nozzle is shown in fig. 1.

Krüger and Marschner's work dealt mainly with another aspect of the subject, *i. e.*, the "edge tones" produced when the vortices strike a concentric edge placed at a distance from the annular slit, but they also gave a few results at low frequency for the simple case with no edge, from which they maintained the law applying to this case to be V/nd = a constant (=18), (d = width of slit, independent of D, the diameter of the disk). As these results seemed to be at variance with what physical notions would suggest, it was decided to examine both aspects of the problem further.

It may be pointed out that the annular mouthpiece finds application in certain sources of sound†, in which the air issuing strikes some form of resonator, notable examples being the Galton whistle, and the "bell whistle" used on locomotives.

Cylindrical Pipes "blown" by Annular Apertures.

The nozzles or mouthpieces used were made to the design described by Krüger and Marschner. Each consisted of a hollow brass cylinder, about 10 cm. long, narrowed at one end for attachment to a rubber tube from the reservoir; a $\frac{1}{8}$ in. brass rod formed the axis of the cylinder and was kept in position by two circular plates, perforated with holes. The brass rod projected a fraction beyond the mouth of the cylinder, and the projection was threaded, so that a washer of slightly less diameter than the inside of the cylinder might be screwed down flush with the mouth, against a stop on the rod. There were two mouthpieces, one of 1·390 cm. inside diameter, provided with two interchangeable disks, 1·254 cm. and 1·200 cm. diameter respectively; the other tube of 2·883 cm. diameter, with washers 2·700 cm. and 2·500 cm. diameter. These were held in a clamp, and a pipe of thin brass tube was filed

* Strouhal, *Ann. der Phys.* v. p. 216 (1878).

† First so used by Gripon, *Ann. der Phys.* viii. p. 384 (1874).

down to a bevel at the mouth, corresponding to the upper lip of an organ pipe of 1·33 cm. diameter for the smaller mouthpiece and 2·80 cm. for the larger. The pipe was set co-axially to the mouthpiece, and the distance "f" between nozzle and lip was measured by a travelling microscope. The blower consisted of a tall tank into which high-pressure water could be run through a regulating tap at the bottom. The only outlet for the air driven out of the tank by the water was by way of the nozzle formed in the mouthpiece, between the brass disk and the cylinder. This air impinging on the lip of the pipe at a suitable speed caused it to sound its fundamental or an overtone. The tone was purer than that of an average diapason of metal, but not so loud, though of sufficient intensity for the frequency to be estimated by comparison with a monochord, beats being easy to count; the tone of the pipe, thus excited, could be kept constant for

TABLE I.

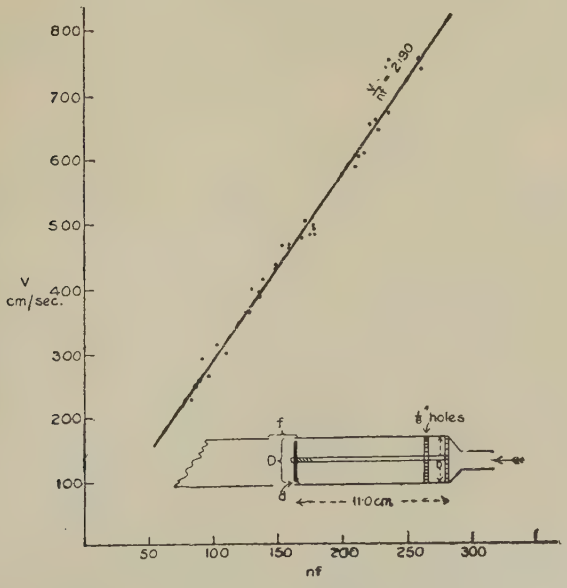
Air Results with Pipe.

Pipe D′.	D (Disk).	d.	f.	n.	V.	$\frac{V}{nf}$.
cm.	cm.	cm.	cm.		cm./sec.	
1·390	1·254	·068	·24	620	476	3·19
			·27	950	736	2·88
			·34	365	354	2·85
			·35	500	490	2·80
			·35	372	385	2·97
			·36	475	476	2·78
			·36	640	668	2·90
			·38	376	429	3·00
			·38	763	793	2·74
			·40	553	657	2·97
			·42	370	460	2·97
			·42	500	602	2·88
			·45	502	639	2·83
			·72	186	379	2·83
1·390	1·200	·095	·34	195	496	2·82
			·34	372	392	3·11
			·42	496	582	2·80
			.42	370	454	2·90
			·52	248	364	2·83
			·52	372	525	2·73
			·58	312	518	2·86
2·883	2·700	·091(5)	·28	283	214	2·66
			·25	433	292	2·70
			·43	223	240	2·50
			·45	285	344	2·69
			·50	190	257	2·73
			·53	283	379	2·51
			·65	155	257	2·55
			·70	180	302	2·40

half a minute or more. The tank was provided with a wide glass water-gauge, so that by observing the rise in, say, 10 seconds, one could calculate the volume "v" of air delivered in that time through the nozzle of area A. Then the velocity of efflux, $V = v/10A$. Thus V, n, D, and f were all known.

The resonance curve is flat, owing to the strong damping, although finer adjustment of wind-speed is needed than that on an ordinary flue pipe. In Table I. the value of V given is that which appeared to elicit the given tone most strongly.

Fig. 1.



These results are shown on fig. 1, where it will be seen that they lie fairly on the line given by $V/nf = 2{\cdot}90$. As all the results for various values of D and d fall on the same line, it appears that these quantities have no appreciable effect on the non-dimensional quantity, V/nf. That the frequency of the pipe was the same as that of the rate of production of vortices was confirmed by mixing smoke with the air and examining the motion stroboscopically. The same value for V/nf was found by Krüger and Marschner using the circular edge, and was explained by them as follows. As each eddy strikes the edge, it sends out a wave

of compression, which travels back to the nozzle with the speed of sound, starting another vortex which travels with the fluid to the edge. The distance between successive vortices thus becomes equal to f or a sub-multiple of f; f is the wave-length of a disturbance of frequency n, which travels from slit to edge. If we assume the translational velocity of the eddies to be always a constant fraction a of V, then $V/nf=a$. The pipe and the eddy system are accordingly "coupled" in the acoustic sense. Experiments in water in which a stream of liquid from a nozzle struck a small length of pipe seemed to show that unless the natural period of the pipe as resonator coincided with that of the vortices, the distance between successive vortices in each row was not forced into coincidence with f; at any rate, with the adjustment possible in the apparatus, no such effect was observed, nor with smoke in air, except at resonance.

Results without Pipe—in Water.

Attention was now turned to the more important case—to us—of the frequency of the eddying produced by outflow from the nozzle into a clear space. Water seemed more amenable as fluid, and previous experiments * on æolian tones had taught us that viscosity was not likely to influence the period of the motion. In order to examine the motion, the issuing fluid was coloured with Meldola's Blue, and the nozzles submerged mouth downwards in a rectangular tank of 10 litres capacity, filled with clear water. V was measured by collecting the water from an overflow pipe, which met the surface of the liquid normally near the top of the tank; n was found by two methods—(1) by counting (when less than 6 per sec.), (2) by looking through a stroboscopic disk. The use of the stroboscope for examining a motion such as this, which, though periodic, does not exactly repeat itself in space, is difficult, but with practice was found to give results in agreement with the first method over the range where they were both applicable (*vide* fig. 2).

The problem of the dependence of the eddy frequency on the dimensions of the nozzle was attacked from two directions. At first, disks of different diameter were used in three nozzles previously described; this meant that both D and d varied. Subsequently a fixed disk was used, outer tubes of different diameters being clamped round it, so that d varied while D was constant.

* Richardson, Proc. Phys. Soc. xxxvi. p. 153 (1924).

The graphs show that there is a critical velocity V_c for each value of d, below which the fluid emerges in a steady

Fig. 2.

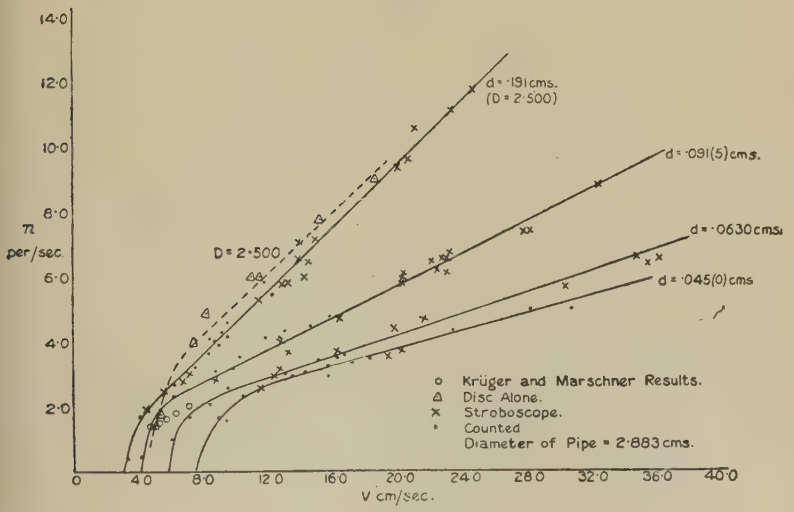
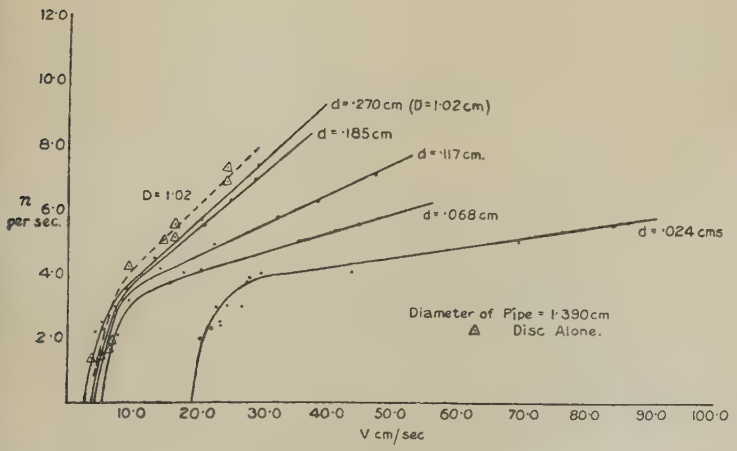


Fig. 3.



stream. From velocities a little above the critical, the relation between V and n becomes linear, the slope, $\frac{\delta V}{\delta n}$, of the line decreasing as d increases, tending to a limiting

Fig. 4.

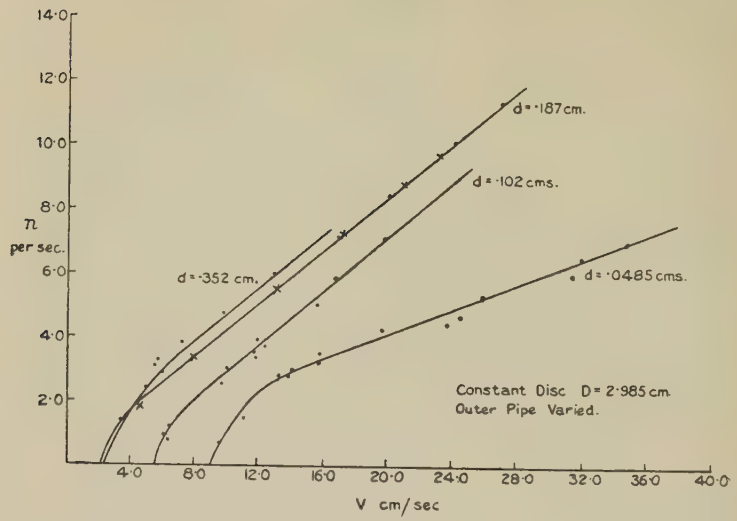
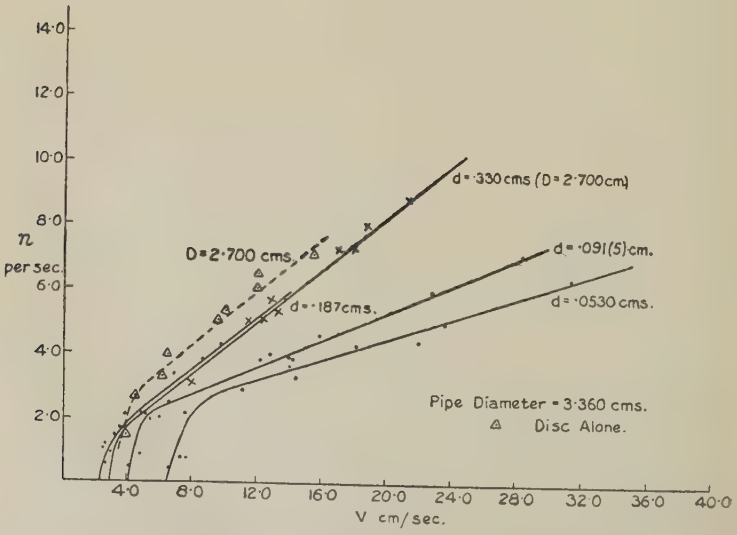


Fig. 5.



constant slope when d reaches 2 mm. The critical velocity is inversely as d, and practically independent of the disk. This indicates a Reynolds' Number of about 40 as the limit

for steady motion in the slit. The graph (fig. 7) includes a few measurements of V in air (mixed with magnesium oxide smoke).

Fig. 6.

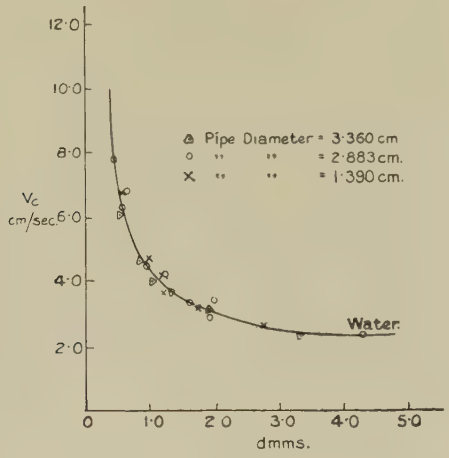
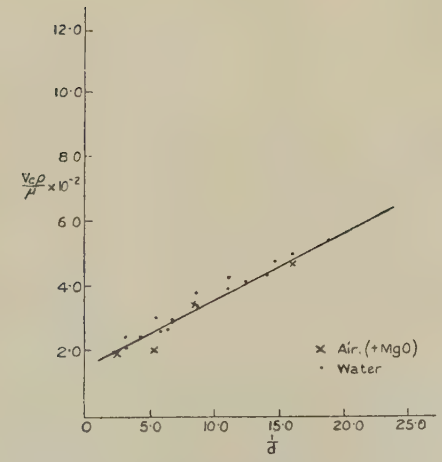


Fig. 7.



Results without Pipe—in Air.

It is difficult to draw any conclusions from observations of air mixed with smoke in the absence of a resonator. The periodic heating and cooling of a hot wire, however, serves to indicate the period of the eddy production, as

was shown by Relf & Simmonds *, who succeeded in thus measuring the value of V/nD for a cylindrical rod past which air is streaming. The wire is heated electrically until nearly red-hot, and is coupled to a shunted vibration galvanometer through a transformer. The galvanometer is tuned to maximum resonance with the period of heating and cooling of the wire, and for determining the corresponding frequency we calibrated the galvanometer with the intermittent current from a make-and-break of the vibrating reed type; the length of the reed was varied, and its frequency found by means of the stroboscope. This was in place of Relf's method of speeding-up an alternator to the desired frequency. The range of n in our experiments was from 30 to 100. The wire consisted of an inch of ·001 in. platinum, mounted horizontally over part of the annular slit. This method does not lead to such accurate results as that of visual observation, as the hot-wire system is not sufficiently sensitive. Results are shown in Table II., and also on fig. 8.

Table II.

Pipe D′.	D (Disk).	d.	$\frac{d}{D}\times 10^2$.	$\frac{\delta V}{\delta n}$.	$\frac{\delta V}{\delta n}\cdot\frac{1}{D}$.
cm.	cm.	cm.			
2·883	2·793	·045	1·61	6·80	2·43
	2·700	·091	3·37	5·00	1·85
	2·500	·191	7·65	2·54	1·01
	2·008	·437	21·90	1·66	·79
3·360	3·253	·053	1·63	8·57	2·65
	3·198	·081	2·54	6·60	2·07
	3·157	·101	3·21	4·00	1·27
	2·985	·187	6·25	3·26	1·09

Explanation of V : *n Curves.*

The fact that, when the width of the slit is considerable, the slope of the linear part of the V : n curve tends to a constant limit, confirms our earlier suggestion that, when the circumference of the disk is at a moderate distance from the outer tube, we are observing the æolian eddies due to the disk placed in the path of the issuing stream. The increase in the slope of these curves as the slit gets smaller must then be attributed to the proximity of the outer walls. The effect is similar to the "interference" due to the walls of a wind-channel encountered in model experiments in aeronautics.

To confirm these conclusions, values of V and n for a disk in an open channel were obtained. In default of a proper water-channel, a large bowl full of water was made to

* Relf & Simmonds, Phil. Mag. xlix. p. 509 (1925).

revolve, while the disk was held below the water and normal to the rotating fluid. Blue liquid, fed in behind the disk, made the vortices visible; and V was found by timing dust particles in the water. This was a rough method, but the results for these disks fell, within the accuracy of the experiment, on the previous V : n curves for wide slits (exceeding 2 mm.) (*vide* figs. 2, 3, 5 : dotted lines).

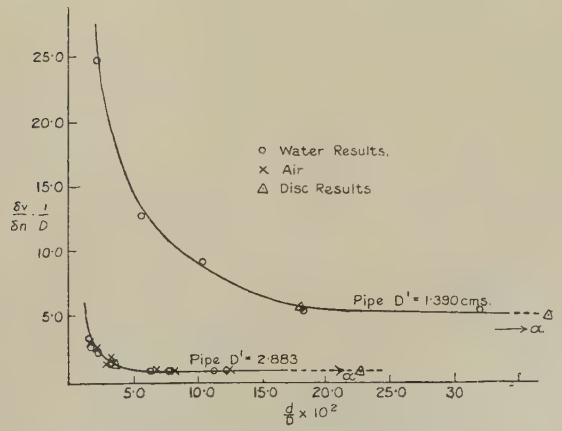
It is of interest to see why Krüger and Marschner were led to a wrong conclusion in this respect. By some misfortune, their results cover just that small part of the curve, near the critical velocity (*vide* fig. 2), where V/nd might be considered constant. The more extended results given here show that this is an anomalous region, the main range of the phenomenon being expressible in terms of Æolian Tones.

Theory.

If we regard the phenomenon as an Æolian Tone effect, modified by interference of the outer tube of the nozzle, we must adopt a formula of the type

$$\frac{\delta V}{\delta n}\,\frac{1}{D}\cdot\phi\left(\frac{d}{D}\right) = \text{constant}. \quad . \quad . \quad . \quad . \quad (1)$$

Fig. 8.



The form of the function $\phi\left(\frac{d}{D}\right)$, which expresses the influence of the boundary, may be determined by plotting $\frac{\delta V}{\delta n}\,\frac{1}{D}$ against $\frac{d}{D}$. This is done in fig. 8.

The results then fall onto two curves: one for the disks used in the narrow nozzle, and one for those in the wider nozzles. (It was impossible to use the set of small

disks in the wide tubes owing to the impossibility of getting symmetrical flow when d exceeds 4 mm.) That all the results do not fall on an unique curve, though each curve has the same shape, is due to lack of constancy in V/nD, even in the open channel. Cylinders in the form of narrow wires exhibit an anomalous high value of V/nD *. To account for this, it is usual, following Lord Rayleigh, to multiply $\frac{\delta V}{\delta n}\frac{1}{D}$ by a function of VD/ν, and such a function would need to be included as a factor in equation (1) to make this equation universally applicable. Only having the two curves, we cannot satisfactorily determine the form of this function, but probably the viscous term would only affect results for small disks.

The relation between $\frac{\delta V}{\delta n}\cdot\frac{1}{D}$ and $\frac{d}{D}$ for either curve of fig. 8 is approximately $\frac{\delta V}{\delta n}\cdot\frac{1}{D}\times\frac{d}{D}=$ constant, for small values of d. So that equation (1) becomes, for narrow slits

$$\frac{\delta V}{\delta n}\cdot\frac{d}{D^2}=K_1, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and for wide slits, simply

$$\frac{\delta V}{\delta n}\frac{1}{D}=K_2,$$

where K_1 and K_2 involve $\frac{VD}{\nu}$ when the diameters of the disks are small.

As regards the influence of the circular edge used in the acoustic observations, we may accept the sound-wave explanation, or we may look for an explanation in the "secondary" eddies produced by friction of the fluid on the sides of the edge. These appear as vortex-rings, alternately one inside and one outside the ring-shaped edge, lying between the vortices arriving from the nozzle, and rotating in the opposite sense. Karman † has shown mathematically that in a series of alternate vortices in a double row, h/l must be a constant for maximum stability, where l = distance between those in a row, and h = distance between the rows (*i. e.*, difference of radii of rings). As the vortices recede from the orifice, h and l are seen to increase, so that the greater the distance from slit to edge, the greater is the separation between the (primary) vortices striking

* Richardson, *loc. cit.*

† Karman, *Gött. Nach.* 1912, p. 547.

the edge. As the secondary eddies have to take their places between the primary ones, this means that l and h, for the set of eddies along the sides of the edge, increase with f. This seems to react in some way on the production of the primary eddies at the nozzle, particularly when some suitable resonator is present. This would account for the reduction of n as f increases, and as V/nf is found to be constant, it would appear that h and l are always proportional to f, which implies that the separation of successive eddies increases regularly with distance from the slit.

This is a tentative suggestion, but is confirmed in part by photographs of eddies produced when water from a linear slit strikes a straight edge*. Such photographs show the secondary vortices plainly; on measuring these photographs we find that the eddies along the edge are closer together when the latter is near the slit. We find the same effect in photographs we have obtained using the annular slit and edge. A recent Paper † has shown that the boundaries of the eddy tracks open out regularly, in the case of the straight slit and edge; (over a considerable range, h, and therefore l, is directly as f).

Summary.

The conclusions of Krüger and Marschner on their work on the frequency of eddies produced in the flow from annular slits require modification. Whereas they ascribe the characteristics of the motion to the width of the slit, we claim to show that the motion once started is governed by the diameter of the disk, modified by the width of the slit, when the latter is small (less than 2 mm. in those we examined). It is, in fact, the Æolian Tone phenomenon of a disk, modified by the outer boundary of the nozzle. There is a critical velocity for the commencement of the eddying flow, which is governed by the slit; but a little above this, at another critical velocity, the pendulation is governed by the size of the disk.

When the eddies strike a circular edge, the results of Krüger and Marschner are confirmed; the distance between successive vortices becomes equal to, or a sub-multiple of, the distance from slit to edge. This is ascribed to the secondary eddies produced at the edge itself.

In conclusion, we wish to give our best thanks to Prof. A. W. Porter, D.Sc., F.R.S., for putting the necessary facilities at our disposal and for encouragement during the course of this research.

* Schmidtke, *Ann. der Phys.* lx. p. 742 (1919).

† Benton, Proc. Phys. Soc. xxxviii. p. 114 (1926).

XXXVI. *Some Considerations of the Reaction Constant Equation, and a Simple Method of Determining the End Point.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

THE method of determining the end point and velocity constant of a monomolecular reaction from two values obtained at specified times such that one time is half the other, which is described by Mr. Robert Christie Smith in your issue, 7th ser. vol. i. p. 496 (1926), was previously developed by Dr. L. N. G. Filon in a somewhat different form, and is described in 'Investigations on the Theory of Photographic Process," by S. E. Sheppard and C. E. K. Mees, p. 65 (Longmans, Green & Co., 1907). The method has been in continued use in practical sensitometry since then.

Using Mr. Smith's nomenclature, the equation $1/t \log \frac{T_\infty}{T_\infty - T} = k$ may be written $T = T_\infty (1 - e^{-kt})$. If T_n and T_{n+1} are chosen so that $t_{n+1} = 2t_n$, then

$$T_n = T_\infty (1 - e^{-kt_n}), \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

$$T_{n+1} = T_\infty (1 - e^{-kt_{n+1}}) ; \quad . \quad . \quad . \quad . \quad (b)$$

and putting $e^{-kt_n} = x$, we have from (a) and (b)

$$\frac{T_n}{T_{2n}} = \frac{1-x}{(1-x^2)} = \frac{1}{1+x} = \frac{1}{1+e^{-kt_n}} ;$$

hence

$$\frac{T_{2n} - T_n}{T_n} = e^{-kt_n}$$

and

$$k = \frac{1}{t_n} \log \frac{T_n}{T_{2n} - T_n},$$

which gives k, and T_∞ may be obtained by substitution.

Mr. Smith's deduction of this method is obviously entirely independent, and is valuable in drawing attention to it anew and commending it to a wider field of utility.

Very truly yours,

S. E. SHEPPARD,

Assistant Director of Research.

Eastman Kodak Company,
Rochester, N.Y.
10 April, 1926.

XXXVII. *Temperature Stresses and Deflexions in the Fins and Barrel of an Air-cooled Internal Combustion Engine Cylinder.* *By* A. M. Binnie, *M.A. Cantab.**

Summary.

In the following paper an attempt is made to evolve a method of calculating the temperature stresses and deflexions in the barrel and radial fins of an air-cooled internal combustion engine cylinder. For the simple case considered it is shown

(1) That much weight can be saved by reducing the thickness of the fins towards their tips. The decrease in cooling power and the increase in temperature stress, which ensue, are both negligibly small.

(2) That the spacing of the fins is of importance. To avoid distortion of the cylinder barrel the fins should be placed as near together as possible compatible with facility of casting.

(3) That to a small extent the temperature stresses in the fins assist the barrel to withstand the internal pressure in the cylinder.

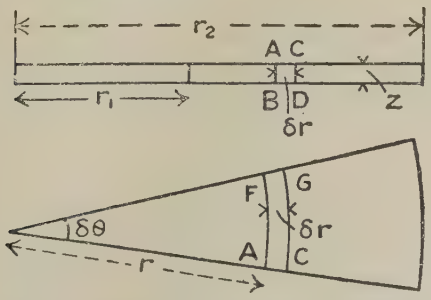
Introduction.

TO avoid complexity, the theoretically perfect case is considered, in which a hot cylinder is steadily giving out heat solely by radiation to its surroundings and obeying Newton's Law of Cooling. The fin is supposed to be thin so that for points equidistant from the cylinder axis the stresses and shift are constant.

In the first instance the fins alone will be considered.

Fin of Constant Thickness.

Fig. 1.



Consider the fin depicted in fig. 1. Taking the element whose plan and elevation are shown by AFGC and ABCD

* Commuicated by the Author.

respectively, the heat-flow outwards across AB is

$$-\mathrm{K}\,.\,r\,.\,\delta\theta\,.\,z\,.\,\frac{d\mathrm{T}}{dr},$$

where K is the coefficient of conduction and T the temperature at radius r measured above that of the surroundings. The heat-flow outwards across CD is

$$-\mathrm{K}(r+\delta r)\delta\theta\,.\,z\,.\,\frac{d}{dr}\left(\mathrm{T}+\frac{d\mathrm{T}}{dr}\,.\,\delta r\right).$$

The loss of heat by radiation is $2e\,.\,\mathrm{T}\,.\,r\,.\,\delta\theta\,.\,\delta r$ where e is the coefficient of emissivity. Hence, equating and simplifying, the T-r relation is given by the equation

$$\frac{d^2\mathrm{T}}{dr^2}+\frac{1}{r}\,.\,\frac{d\mathrm{T}}{dr}-\frac{2e\mathrm{T}}{\mathrm{K}z}=0,$$

of which the solution is

$$\mathrm{T}=\mathrm{AJ}_0\left(ri\sqrt{\frac{2e}{\mathrm{K}z}}\right)+\mathrm{BH}_0\left(ri\sqrt{\frac{2e}{\mathrm{K}z}}\right).$$

A and B are constants given by the relations that at $r=r_1$, $\mathrm{T}=\mathrm{T}_1$, and at $r=r_2$, $\frac{d\mathrm{T}}{dr}=0$.

For a short fin the loss of heat from the tip becomes of importance, and a trial and error procedure is necessary, the two constants being chosen so that at $r=r_1$, $\mathrm{T}=\mathrm{T}_1$, and at $r=r_2$, $\frac{d\mathrm{T}}{dr}=-\frac{\mathrm{E}z\mathrm{T}_2}{\mathrm{K}}$. In all practical cases, however, this further complication is an unessential refinement.

Proceeding to a consideration of the temperature stresses, let u, p, and t be the shift, radial tensile stress, and hoop tensile stress respectively at radius r. The fin is assumed thin, so that there are no appreciable longitudinal stresses. Then the stress-strain relations are given by

$$\mathrm{E}\left(\frac{du}{dr}-k\mathrm{T}\right)=p-\frac{t}{m}$$

and

$$\mathrm{E}\left(\frac{u}{r}-k\mathrm{T}\right)=t-\frac{p}{m},$$

and the equation of equilibrium of the element by

$$p-t+r\,.\,\frac{dp}{dr}=0,$$

k being the coefficient of thermal expansion, E Young's

Modulus, and m Poisson's Ratio. Hence, using the temperature relation already found,

$$p = \frac{iEk}{r\sqrt{\frac{2e}{Kz}}}\left[AJ_1\left(ri\sqrt{\frac{2E}{Kz}}\right)+BH_1\left(ri\sqrt{\frac{2E}{Kz}}\right)\right]+\frac{F}{2}+\frac{D}{r^2},$$

F and D being constants determined by a knowledge of the radial pressures existing at the root and tip of the fin. It will be noticed that the terms involving F and D are the same as those which give the distribution of radial stress in a fin whose temperature is the same throughout. Further,

$$t = F-EkT-p, \quad \text{and} \quad u = \frac{r}{E}\left[F-p\left(1+\frac{1}{m}\right)\right].$$

Fin of Varying Thickness.

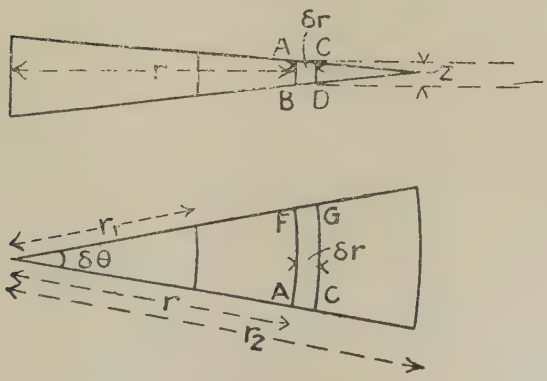
Using the same notation and considering the element shown in fig. 2, it is evident that the heat-flow outwards across AB is

$$-K \,.\, r \,.\, \delta\theta \,.\, z\frac{dT}{dr},$$

and across CD is

$$-K(r+\delta r)\,\delta\theta\left(z+\frac{dz}{dr}\delta r\right)\frac{d}{dr}\left(T+\frac{dT}{dr}\delta r\right).$$

Fig. 2.



The heat lost by radiation is $2 \,.\, \delta r \,.\, \delta\theta \,.\, e \,.\, T \,.\, r$, if $\frac{dz}{dr}$ may be assumed small. Hence the T-r relation is

$$\frac{d}{dr}\left(zr\frac{dT}{dr}\right)+2eTr = 0.$$

The constants in the solution of this equation are found, as before, from the facts that at $r=r_1$, $T=t_1$, and at $r=r_2$, $\frac{dT}{dr}=0$. If extreme accuracy is desired, the second condition should be that at $r=r_2$, $\frac{dT}{dr}=\frac{-ezT}{K}$.

Consider in the first instance a fin whose thickness varies inversely as the radius. If $z=\frac{\lambda}{r}$, λ being a constant, the equation connecting T and r becomes

$$\frac{d^2T}{dr^2}-PTr=0, \quad \text{where} \quad P=\frac{2e}{\lambda K}.$$

The solution of this is

$$T=r^{\frac{1}{2}}\left[AJ_{\frac{1}{3}}\left(\tfrac{2}{3}iP^{\frac{1}{2}}x^{\frac{3}{2}}\right)+BJ_{\frac{1}{3}}\left(\tfrac{2}{3}iP^{\frac{1}{2}}x^{\frac{3}{2}}\right)\right],$$

where A and B are constants ; but a solution in a form more convenient in the subsequent stress determinations can be found without the aid of Bessel Functions. Let

$$T=a_0+a_1r+a_2r^2+\ldots+a_nr^n.$$

Then, by equating coefficients of like powers of r,

$$T=a_0\left[1+\frac{Pr^3}{6}+\frac{P^2r^6}{180}+\frac{P^3r^9}{12960}\ldots+\ldots\right]$$
$$+a_1r\left[1+\frac{Pr^3}{12}+\frac{P^2r^6}{504}+\frac{P^3r^9}{45360}+\ldots\right],$$

a series which is seen to be convergent. Since P is in most cases small *, it is sufficient to take

$$T=a_0\left[1+\frac{Pr^3}{6}\right]+a_1r\left[1+\frac{Pr^3}{12}\right],$$

the constants being determined as before.

The stress-strain relations are again

$$E\left(\frac{du}{dr}-kT\right)=p-\frac{t}{m}$$

and

$$E\left(\frac{u}{r}-kT\right)=t-\frac{p}{m},$$

and the equation of equilibrium $zt=\frac{d}{dr}(zrp)$ becomes

$$t=r\frac{dp}{dr}.$$

* In the numerical example taken, P=·00069639 and the maximum value of Pr^3 is ·50767.

Eliminating and simplifying, the p-r equation is given by

$$r^2\frac{d^2p}{dr^2}+2r\frac{dp}{dr}-p\left(1+\frac{1}{m}\right)=-r\mathrm{E}k\left(\frac{\mathrm{P}r^3}{2}a_0+a_1\left(1+\frac{\mathrm{P}r^3}{3}\right)\right).$$

The complete solution of this is

$$\mathrm{P}=\mathrm{Y}_1r^{\cdot745}+\mathrm{Y}_2r^{-1\cdot745}+\alpha r+\beta r^3+\gamma r^4,$$

where

$$\alpha=\frac{-\mathrm{E}ka_1}{\cdot7},$$

$$\beta=\frac{-\mathrm{E}k\mathrm{P}a_0}{21\cdot4},$$

$$\gamma=\frac{-\mathrm{E}k\mathrm{P}a_1}{56\cdot1},$$

and Y_1 and Y_2 are constants. $m=\frac{10}{3}$.

Similarly,

$$t=\cdot745\mathrm{Y}_1r^{\cdot745}-1\cdot745r^{-1\cdot745}+\alpha r+3\beta r^3+4\gamma r^4$$

and

$$u=\frac{r}{\mathrm{E}}[\cdot445\mathrm{Y}_1r^{\cdot745}-2\cdot045r^{-1\cdot745}+\cdot7\alpha r+2\cdot7\beta r^3+3\cdot7\gamma r^4+\mathrm{E}k\mathrm{T}].$$

To compare with these results the further case has been taken of a fin whose thickness varies inversely as the square of the radius. Taking $z=\frac{\lambda}{r^2}$, the general equation becomes

$$\frac{d}{dr}\left(\frac{1}{r}\cdot\frac{d\mathrm{T}}{dr}\right)=\frac{2e}{\lambda\mathrm{K}}\cdot\mathrm{T}r,$$

of which the solution is

$$\mathrm{T}=\mathrm{A}\sinh\mathrm{F}r^2+\mathrm{B}\cosh\mathrm{F}r^2,$$

where $\mathrm{F}=\sqrt{\frac{e}{2\lambda\mathrm{K}}}$ and A and B are constants. Proceeding in a manner similar to that used previously, p is found to be given by the equation

$$r^2\frac{d^2p}{dr^2}+r\frac{dp}{dr}-2p\left(1+\frac{1}{m}\right)=-2Ek\mathrm{F}r^2(\mathrm{A}\cosh\mathrm{F}r^2+\mathrm{B}\sinh\mathrm{F}r^2).$$

The particular integral of this equation cannot be found exactly in a convenient form ; but since F is small, $\sinh\mathrm{F}r^2$ and $\cosh\mathrm{F}r^2$ can be expanded and a solution obtained to any

desired degree of accuracy*. If the bracket in the right-hand side of the above equation be taken as $A\left(1+\frac{F^2r^4}{2}\right)+BFr^2$, then

$$p = Y_1r^{1\cdot612}+Y_2r^{-1\cdot612}+\alpha r^2+\beta r^4+\gamma r^6,$$

where

$$\alpha = -\frac{A}{1\cdot4}\cdot 2EFk,$$

$$\beta = -\frac{BF}{13\cdot4}\cdot 2EFk,$$

$$\gamma = -\frac{AF^2}{66\cdot8}\cdot 2EFk,$$

and Y_1 and Y_2 are constants.

Further,

$$t = \cdot612Y_1r^{1\cdot612}-2\cdot612Y_2r^{-1\cdot612}+\alpha r^2+3\beta r^4+5\gamma r^6$$

and

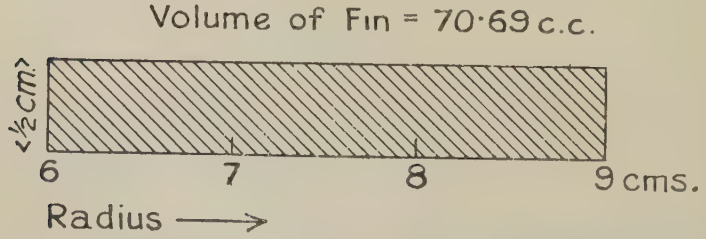
$$u = \frac{r}{E}[\cdot312Y_1r^{1\cdot612}-2\cdot912Y_2r^{-1\cdot612}+\cdot7\alpha r^2+2\cdot7\beta r^4 +4\cdot7\gamma r^6+EkT].$$

It will be seen that in general it is impossible to determine the stresses for any given shape of fin, since it is always necessary to solve two dependent differential equations—the T-r equation and the p-r equation.

Curves (figs. 3–12) are shown, giving the temperature and stress variations in each of the three forms of fin considered,

Fin of Constant Thickness.

Fig. 3.—Cross-section of Fin.



which are supposed of cast iron. In each case, the inner and outer radii are 6 and 9 cm. respectively, the fin thickness at its root is 0·5 cm., the fin temperature at its root is 400° C., the temperature of the surroundings is 0° C., and the fin is assumed to be unconstrained at both root and tip.

* In the numerical example taken, $F=\cdot0054$; and the maximum value of Fr^2 used is ·43632, for which $\sinh Fr^2=45030$, $\cosh Fr^2=1\cdot09670$, and $(1+F^2r^4/2)=1\cdot09519$. The effect of the approximation on the temperatures in the fin is shown in fig. 11.

Fig. 4.—Temperature Drop in Fin.

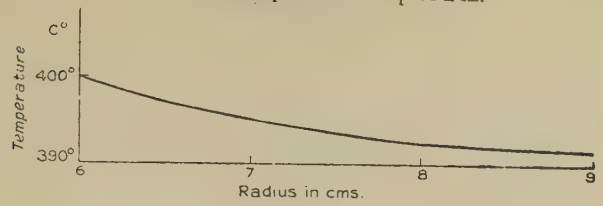


Fig. 5.—Radial Compressive Stress.

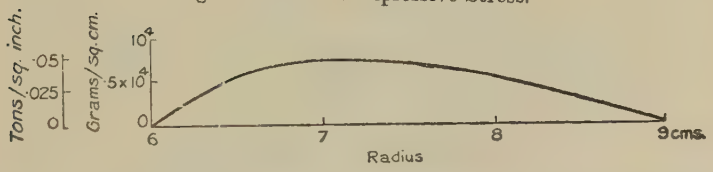
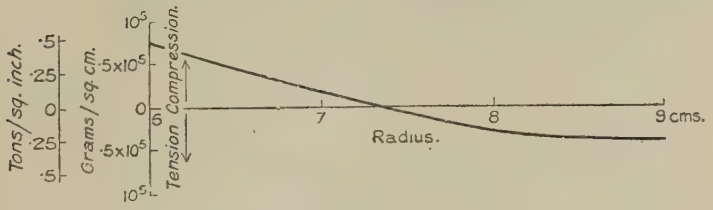


Fig. 6.—Hoop Stress.



FIN WHOSE THICKNESS VARIES INVERSELY AS THE RADIUS.

Fig. 7.—Cross-section of Fin.

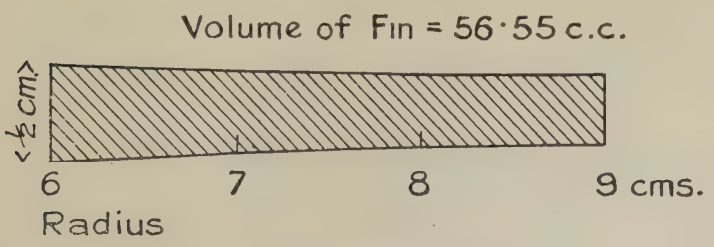


Fig. 8.—Temperature Drop in Fin.

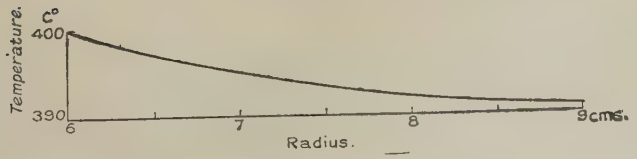
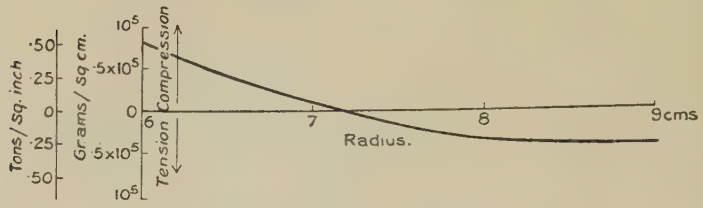


Fig. 9.—Hoop Stress.



FIN WHOSE THICKNESS VARIES INVERSELY AS THE SQUARE OF THE RADIUS.

Fig. 10.—Cross-section of Fin.

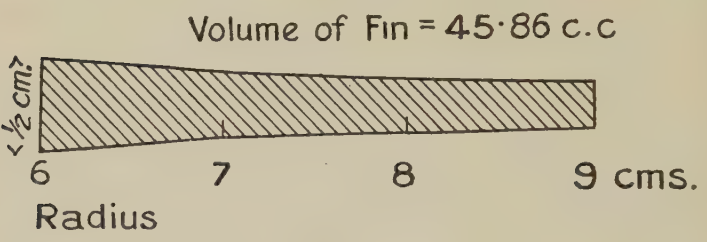
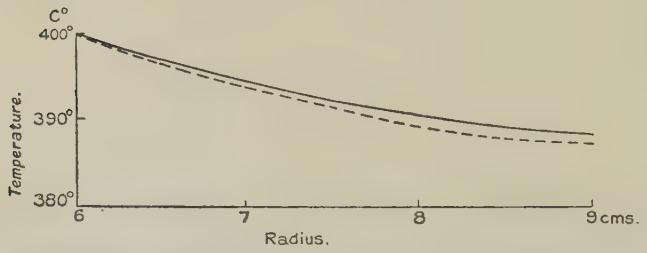
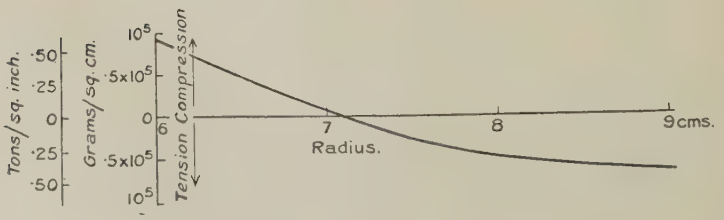


Fig. 11.—Temperature Drop in Fin.



Full line shows Exact Temperature, and broken line shows Approximate Temperature taken.

Fig. 12.—Hoop Stres



The radial pressure curve for the first case only is shown, as it is found that this stress varies but slightly with the shape of the fin and is in any case negligibly small.

These three sets of curves are intended to indicate the order of the stresses developed, and to show to what extent the temperature drops and the stresses increase when the weight of the fin is diminished by a reduction in its thickness towards the tip. It will be seen that the stresses are in no case large and do not increase inordinately when the fin thickness is diminished. The amount of heat dissipated in each case does not materially alter, varying as it does from 16·73 calories per second for the first type to 16·65 calories per second for the third, although the decrease in the weight of the fin is 35 per cent.

The Physical Constants used are:

Coefficient of Emissivity
= ·00015 calorie per second per sq. cm. per degree centigrade.

Coefficient of Conductivity
= ·1436 calorie per second per sq. cm. per degree centigrade per cm.

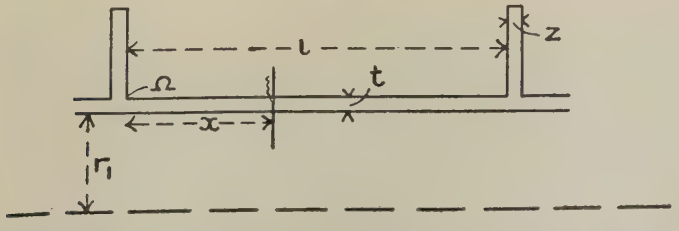
Young's Modulus
$= 1{\cdot}25 \times 10^9$ grammes per sq. cm., equivalent approx. to 8000 tons per sq. inch.

Coefficient of Linear Expansion
$= 10{\cdot}8 \times 10^{-6}$ per degree centigrade.

Stresses and Displacements in a Cylinder Barrel.

After the stresses and shifts in a single fin have been determined, it is possible by means of an extension of Professor Cook's method * to find the stress distribution

Fig. 13.



* Professor Gilbert Cook, D.Sc., "The Distribution of Stress in a Flanged Pipe." Complex Stress Distributions in Engineering Materials. Committee's Report, British Association, 1921. See also Von Sanden, 'Engineering,' Jan. 18th, 1924, p. 87, and Feb. 8th, 1924, p. 173.

and displacements in a cylinder barrel carrying a number of these fins equally spaced. (Fig. 13.)

Let t be the thickness of the barrel assumed small in comparison with r_1 the mean radius ;

y ,, the radial displacement of the wall ;

q ,, the tensile circumferential stress ;

f ,, the tensile longitudinal stress in the barrel at any point distant x measured along the axis from the fixed point Ω ;

P_1 ,, the internal pressure ;

z_0 ,, the root thickness of the fins ;

T_1 ,, the temperature of the barrel, which is equal to the fin root temperature.

The stress-strain relation gives

$$\mathrm{E}\left(\frac{y}{r_1}-k\mathrm{T}_1\right)=q-\frac{f}{m}\text{ ; but }f=\frac{r_1\mathrm{P}_1}{2t}.$$

Hence

$$q=\mathrm{E}\left(\frac{y}{r_1}+\frac{\mathrm{P}_1 r_1}{2tm\mathrm{E}}-k\mathrm{T}_1\right).$$

Considering the equilibrium of a longitudinal strip of the barrel subtending an angle $\delta\phi$ at the axis, the load per unit length due to the internal pressure is $\mathrm{P}_1 r_1\delta\phi$ and due to circumferential stress is $qt\delta\phi$; so that the total load w per unit length is $\mathrm{P}_1 r_1\delta\phi - qt\delta\phi$. The equation connecting load and displacement is

$$\beta\frac{d^4y}{dx^4}=w,$$

where β is the flexural stiffness, which in this case is $\frac{m^2}{m^2-1}\cdot\mathrm{E}\cdot\frac{1}{12}r_1\delta\phi t^3$. Hence, equating and simplifying,

$$\frac{d^4y}{dx^4}+4n^4y=b,$$

where

$$4n^4=\frac{12}{t^2r_1^2}\cdot\frac{m^2-1}{m^2},$$

$$b=\frac{12}{\mathrm{E}r_1t^3}\cdot\frac{m^2}{m^2-1}\left[\mathrm{P}_1r_1\left(1-\frac{1}{2m}\right)+\mathrm{E}k\mathrm{T}_1t\right],$$

and

$$\frac{b}{4n^4}=\mathrm{P}_1\left(1-\frac{1}{2m}\right)\frac{r_1^2}{\mathrm{ET}}+r_1k\mathrm{T}_1$$

$$=y_1,\text{ the radial displacement of the barrel without fins.}$$

The solution of this equation is

$$y = y_1 + \cos nx\,(\mathrm{A}\cosh nx + \mathrm{B}\sinh nx) + \sin nx\,(\mathrm{C}\cosh nx + \mathrm{D}\sinh nx),$$

where the four constants can be found from the facts that $x=0$ and $x=6$, $\frac{dy}{dx}=0$ and $y=y_0$, the radial displacement of the root of the fin. It is assumed that under the fin the barrel is held so that no angular movement is permitted. Hence

$$y = y_1 - (y_1 - y_0)[\cosh nx \cos nx - \mathrm{H}\sinh nx \cos nx + \mathrm{H}\cosh nx \sin nx - \mathrm{L}\sinh nx \sin nx],$$

where

$$\mathrm{H} = \frac{\cosh nl - \cos nl}{\sinh nl + \sin nl},$$

and

$$\mathrm{L} = \frac{\sinh nl - \sin nl}{\sinh nl + \sin nl}.$$

It now remains to determine y_0. Let the shearing force in the barrel at Ω be F per unit length measured along the circumference, acting outwards on the fin. Then the equivalent pressure on the fin is $\mathrm{P}_1 + \frac{2\mathrm{F}}{z_0}$.

But

$$\mathrm{F} = -\mathrm{E}\cdot\frac{m^2}{m^2-1}\cdot\frac{t^3}{12}\cdot\left(\frac{d^3y}{dx^3}\right)_{x=0}.$$

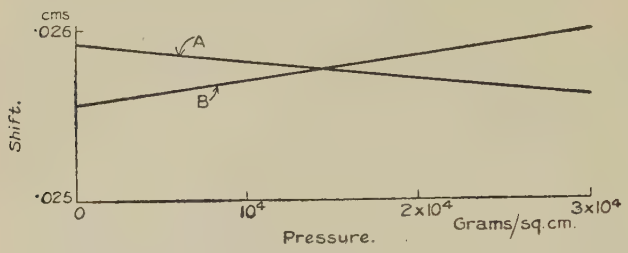
Hence P_2, the equivalent pressure,

$$= \mathrm{P}_1 + \frac{2\mathrm{E}}{3z_0}\cdot\frac{m^2}{m^2-1}\cdot t^3n^3(y_1 - y_0).$$

Therefore for any particular cylinder and under given conditions of temperature and internal pressure, a curve connecting P_2 and y_0 may be drawn. It has been shown how, for any of the fins whose stress distributions and shift functions have been investigated, a curve may be drawn connecting p_1 the internal pressure and u_{r_1} the displacement at the root of the fin. But P_2 must equal p_1 and y_0 must equal u_{r_1}. Hence the point of intersection of the two curves will give these four quantities; and when these are known, all the stresses and displacements both in the fin and in the barrel can be determined.

Figs. 14–21 have been calculated for a cast-iron barrel, ·5 cm. thick and 6 cm. mean radius, on which are cast a

Fig. 14.—Determination of Pressure between Fin and Barrel.

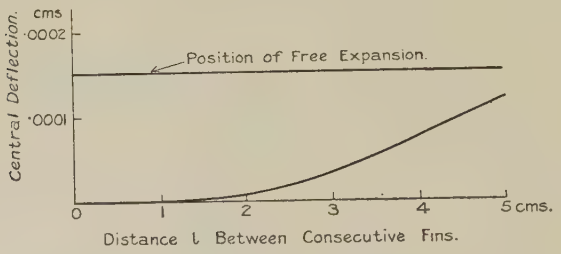


Curve A shows relation between Pressure and Deflexion of Cylinder Barrel.

Curve B shows relation between Pressure and Deflexion of Root of Fin.

Pressure between Fin and Barrel = 14·500 grams/sq.cm.
= 1/10 ton/sq. inch approx.

Fig. 15.—Deflexions of Points midway between adjacent Fins for varying Fin Spacings.



Deflexions are measured from final position of Root of Fin.
Deflexion of Root of Fin = ·02577/cm.

Fig. 16.—Compressive Circumferential Stress at Points midway between adjacent Fins for varying Fin Spacings.

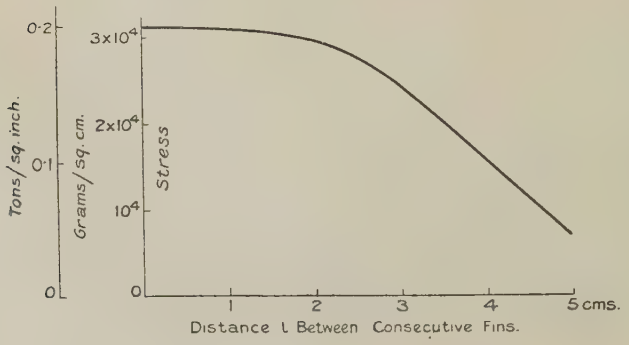


Fig. 17.—Deflexion of Barrel relative to Roots of Fins when Fins are 1 cm. apart.

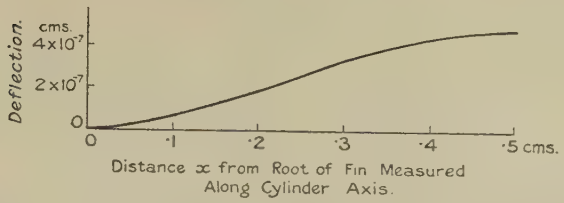


Fig. 18.—Deflexion of Barrel relative to Roots of Fins when Fins are 2 cm. apart.

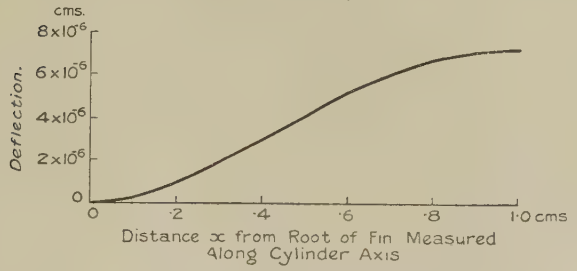


Fig. 19.—Deflexion of Barrel relative to Roots of Fins when Fins are 3 cm. apart.

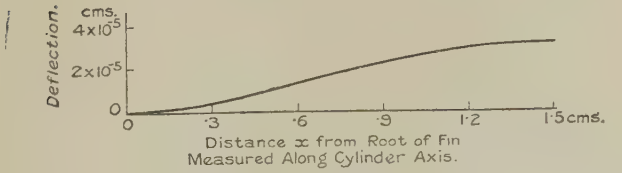


Fig. 20.—Hoop Stress in Fin.

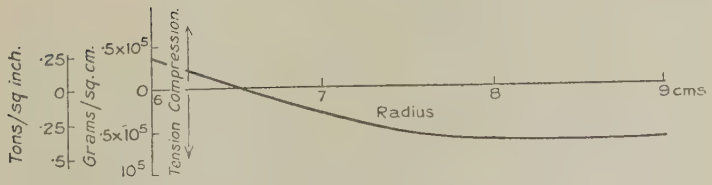
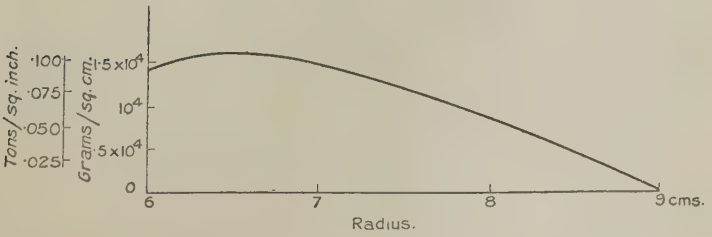


Fig. 21.—Radial Stress in Fin.



number of fins of constant thickness whose dimensions and temperature distributions are the same as those of the fin considered in figs. 3–6. The barrel and the roots of the fins are maintained at a steady temperature of 400° C., and the internal pressure is zero. Fig. 14 shows how the pressure between the cylinder barrel and the root of the fin is determined by the intersection of two pressure-deflexion curves—one for the root of the fin and the other for the barrel. The pressure is found to be about 1/10 ton per sq. inch. Fig. 15 indicates the rapidity with which the deflexion of the barrel at points midway between the fins increases as the distance between the fins increases. This illustrates the importance of spacing the fins closely if an even surface in the cylinder is to result. At the same time it must be remembered that closely spaced fins cause comparatively high circumferential stresses in the barrel, as is clearly demonstrated by fig. 16. Professor Gilbert Cook has shown that under certain circumstances the deflexion of the barrel may exceed the deflexion of the barrel without fins, the condition being $\frac{3\pi}{4n} < x < \frac{7\pi}{4n}$. In the example under consideration this gives values of x lying between 3·18 cm. and 7·41 cm., distances which are too large to occur in normal practice. In any event, the extra deflexion to be expected is not more than 5 per cent. Figs. 17–19 show the deflexions of the barrel relative to the roots of the fins when the fins are 1, 2, and 3 cm. apart respectively. The forms which the barrel assumes are similar but of widely differing magnitudes, the deflexion scales being 100 : 10 : 1. These forms closely resemble those which occur when a barrel of uniform temperature reinforced by external flanges is subjected to internal pressure *, although there is an important change in the stress distribution. For the hot barrel the circumferential stresses are compressive, and decrease as the distance from a fin increases ; while in the other case the reverse ensues, the circumferential stresses, which are tensile, being at a maximum at points midway between the fins. And further, increase in the distance between consecutive fins in the former case decreases the circumferential stress, and in the latter increases it. Finally, figs. 20 and 21 indicate the stresses in the fins.

* Professor Gilbert Cook, *loc. cit.* p. 304.

XXXVIII. *The Photoelectric Emission from Platinum as Influenced by Heating.* *By* Lars A. Welo, *Ph.D.**

THIS paper is intended to be in the nature of a reply to a recent one of Kurt Herrmann † in *Annalen der Physik* on "The Influence of Gas Content on the Photoelectric Emission and the Electrical Conductivity of Platinum." He comes, naturally, to the very controversial question as to whether or not the photoelectric effect for this metal vanishes on the complete elimination of the occluded gases. My ‡ own experiments of 1922, from which I concluded that platinum remains sensitive photoelectrically, are justly criticised on the ground that the temperatures I used were not sufficiently high to secure even moderate elimination of the gases. These experiments of mine were repeated as long ago as February to May, 1923, and it became apparent at once that the photoelectric sensitiveness of platinum becomes gradually less as the temperature at which platinum is heated is increased. Herrmann and I are now, therefore, in complete agreement on this question as far as the experimental facts are concerned. I do not purpose to discuss the meaning of this result beyond presenting rather rough preliminary data on the effect of scraping, which may be interpreted as an indication that surface impurities are developed during the heating.

The results to be presented will show that the ease with which platinum may be made relatively insensitive towards ultra-violet light is very markedly dependent on the sample of platinum employed. My experiments of 1922 were made on a foil which retained its maximum sensitiveness after heating for many hours at a temperature of 1300° C. In the experiments reported on here, a foil was employed which decreased in sensitiveness to about 1/12 of a previous maximum after having been heated to slightly more than 1400° C. Data are presented for another foil which decreased in sensitiveness to 1/37 of a previous maximum value on heating to only 1140° C.

The possible influence of mercury vapour will also be taken up. Herrmann considers that a certain minimum which appears in a curve showing the photoelectric sensitiveness as a function of the heating current sent through the foil is due to the presence of mercury vapour. It will

* Communicated by the Author.

† Herrmann, *Ann. der Phys.* lxxvii. p. 503 (1925).

‡ Welo, Phil. Mag. xlv. p. 593 (1923).

be pointed out that this minimum disappears as the heating is continued or if the temperature is raised, in spite of the continued presence of mercury vapour. It will also be shown that this minimum appears when somewhat similar experiments are performed in the open air and under conditions such that no mercury vapour can possibly be present. Finally, a few curves are included which show that the effect of adding gases after outgassing by heating is dependent on the particular sample of platinum in use.

The Experimental Procedure and the Apparatus.

The experiments were conducted in the same manner as before. The foil was heated with various increasing heating currents, and the photoelectric current was measured after the metal had become cool. After the first "run" on a new specimen, a run was made with successively decreasing heating currents. This is indicated by the arrows on the figures. Two minutes instead of ten was adopted as the standard time of heating with a given heating current during a run.

The tube was similar to that shown in fig. 2 of my previous paper *. Its diameter was half again as great. It had two side tubes instead of one. The second side tube made possible the determination of the temperatures with an optical pyrometer which had been previously calibrated so as to give the true temperature of platinum. The cylindrical receiving electrode of sheet nickel was placed vertically within the main part of the tube so as completely to surround the foil. Two narrow slits were cut on opposite sides of this electrode, which was placed so that the slits were in line with the side tubes. The parts of the tube near the foil were always baked, while pumping, at 350° C. for two or three hours before making the first run on a new foil. When heating-currents were sent through the foil the pressures increased to as much as 5×10^{-5} mm. of mercury, but when the foil was not being heated the pressure while pumping was constantly of the order 10^{-6} mm., as measured with a McLeod gauge in connexion with the tube through a liquid-air trap. Liquid air was applied to this trap before inserting the foil and sealing up, and was kept in place continually until the work with that foil was complete. As the work on a foil extended over a long time (35 days in one case) the pump was not run all the time. Over-night the pressures sometimes rose to 9×10^{-5} mm., but usually this over-night

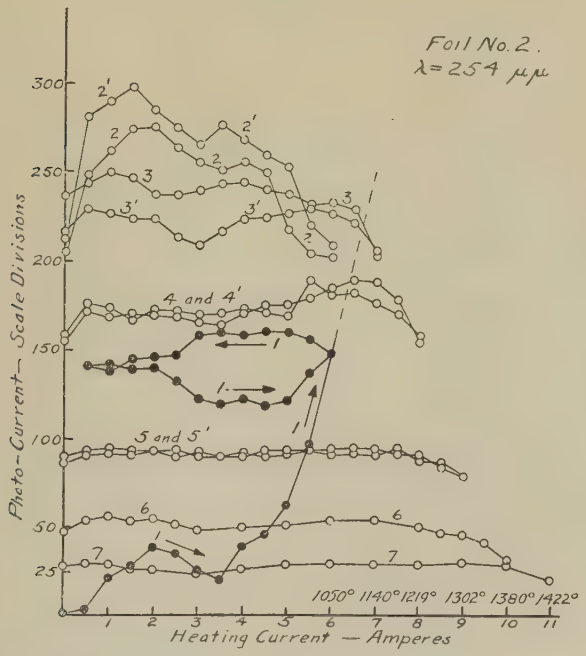
* *Loc. cit.*

increase was to 2×10^{-5} mm. The lines near 254 $\mu\mu$ from a quartz mercury arc were used exclusively for the work reported upon. The foils were 13 cm. long, 0·5 cm. wide, and 0·001 cm. thick.

The Decrease of Sensitiveness on Heating at High Temperatures.

Fig. 1 shows the results obtained with Foil No. 2, the complete history of the foil during the experimental work

Fig. 1.



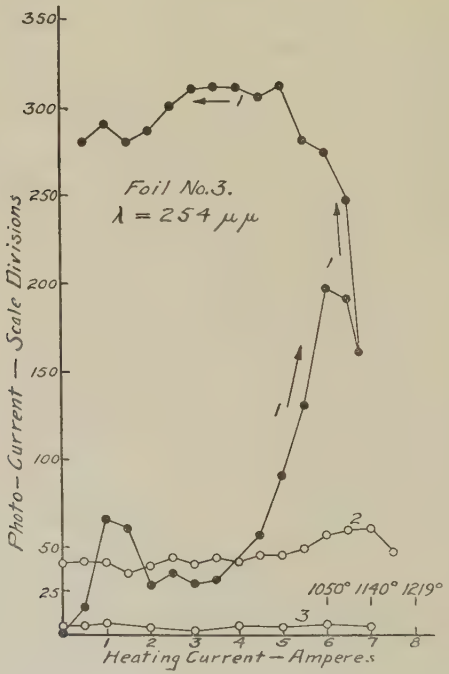
1. Original runs on new foil.
2. Immediately after total heating of 110 minutes with 6 amperes, 1050° C.

2'.	,,	,,	,,	240	,,	,, 6	,,	1050° C.
3.	,,	,,	,,	60	,,	,, 7	,,	1140° C.
3'.	,,	,,	,,	480	,,	,, 7	,,	1140° C.
4.	,,	,,	,,	60	,,	,, 8	,,	1219° C.
4'.	,,	,,	,,	180	,,	,, 8	,,	1219° C.
5.	,,	,,	,,	60	,,	,, 9	,,	1302° C.
5'.	,,	,,	,,	120	,,	,, 9	,,	1302° C.
6.	,,	,,	,,	80	,,	,, 10	,,	1380° C.
7.	,,	,,	,,	40	,,	,, 11	,,	1422° C.

being given in the caption accompanying the figure. To this history as given in the caption it is only necessary to add that between runs 1 and 2 when the foil was being heated with 6 amperes, T = 1050° C., the heating-current

was accidentally raised to nearly 7 amperes, T=1140° C., for about three minutes. It is assumed that the greater sensitiveness throughout run 2 as compared with the maximum of run 1 is due to this cause. It is on this assumption that the first part of run 1 is extrapolated along the broken line. In this section of this paper, no data are shown for Foil No. 1 as it was used in the preliminary work of adjusting the electrometer sensibility, slit-width, high resistance, &c. to convenient values. The general

Fig. 2.



1. Original runs on new foil.
2. Immediately after total heating of 180 minutes with 6 amperes, 1050° C.
3. „ „ „ 60 „ „ 7 „ 1140° C.

behaviour was the same as with Foil No. 2. After having been heated for 150 minutes at a temperature of 1416° C., its sensitiveness was still 1/13 of the previous maximum value.

Foil No. 3, which came from the same supply as Foils Nos. 1 and 2, proved to be strikingly different in its behaviour. This foil, too, became less sensitive to $\lambda=254\ \mu\mu$, but this insensitive condition could be brought about much

more easily. This is shown in fig. 2. After heating to only 1140° C., the sensitiveness was reduced to 1/37 of a previous high value. I do not recall nor do my notes indicate any conditions different from those existing when Foil No. 2 was being studied. The pressures were about 10^{-6} while pumping, and the over-night increase was to 8×10^{-5}, which is slightly less than that observed with Foil No. 2 during the early part of the work with that foil.

It is clear from these results that I cannot now maintain my previous conclusion that the photoelectric effect does not tend towards zero if platinum is heated in a vacuum of the order of 10^{-6} mm. of mercury at sufficiently high temperatures. On this point, as an experimental fact, I am in complete agreement with Herrmann and the other workers of the Hallwachs-Wiedemann group. I am likewise in accord with Tucker * and Woodruff †, who have conducted similar work in this country. The results shown in figs. 1 and 2 explain much of the disagreement which has existed in this field. For example, in my previous work I heated at 1300° C. and observed no tendency for the photoelectric current to become smaller. I did not go beyond 1300° C. because evaporation of platinum becomes marked there, and evaporation is to be avoided if one wishes to heat for a long time. In the present experiments, heating at 1300° C. decreased the sensitiveness to about a third, as shown in runs 5 and 5′ of fig. 1. With still another foil, No. 3 of fig. 2, the effect had fallen to 1/37 on heating to only 1140° C. Small amounts of impurities of an unknown nature undoubtedly play an important part in the results obtained.

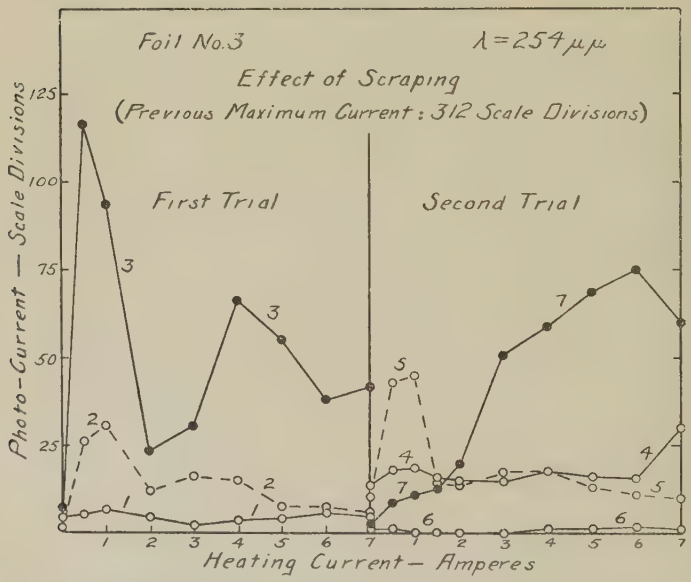
Scraping to remove possible Surface Impurities.

It is perfectly natural to attribute the smaller photoelectric sensitiveness of platinum after heating at high temperatures to the smaller concentration of occluded gases, in view of the fact that gases are continually being driven off during the heating. This has been the usual explanation. It is not in complete accord with the manner in which photoelectric sensitiveness is recovered, as has recently been pointed out by Woodruff ‡. Nor is it in accord with the appearance of a relatively insensitive condition when one heats platinum in the region of 100° to 500°, as has been

* Tucker, Phys. Rev. xxii. p. 574 (1923).
† Woodruff, Phys. Rev. xxvi. p. 655 (1925).
‡ *Loc. cit.*

observed by Herrmann * and myself † when the heating is done in a vacuum, and by Zeleny ‡ and Davidson § when the experiment is conducted out in the open at atmospheric pressure. It is hard to avoid a suspicion that some insensitive surface condition is built up during the heating, in spite of the best vacuum conditions and careful choice and preliminary handling of the platinum. There is wide room for speculation as to the structure of this insensitive layer. It was with the possibility in mind that the surface might be chemically different from the body of the platinum, that I

Fig. 3.



1. Same as run 3, fig. 2.
2. Immediately after standing in air 1 hour.
3. „ „ scraping.
4. „ „ heating 60 minutes with 7 amperes, 1140° C.
5. „ „ standing in air 1 hour.
6. „ „ heating 120 minutes with 7 amperes, 1140° C.
7. „ „ scraping.

undertook to scrape the metal after it had been made nearly insensitive towards radiation of wave-length $\lambda = 254\ \mu\mu$. The tests were made on Foil No. 3 directly after taking run 3 of fig. 2. The runs shown in fig. 3 are consecutive.

* *Loc. cit.* † *Loc. cit.*

‡ Zeleny, Phys. Rev. xii. p. 321 (1901).

§ Davidson, Phys. Rev. xxvi. p. 1 (1908).

It was necessary to make a comparison with the effect of mere exposure to air, since the scraping had to be done out in the open. To remove the foil, scrape, replace and re-exhaust took about an hour, so that previous to the comparison runs the foil was exposed to air for about the same length of time. Runs 3 and 7 were made after scraping. These experiments are admittedly rough, and the results are not concordant between themselves. But it is significant that after scraping the foil is, on the whole, more sensitive than after mere exposure to air.

This scraping experiment should be done in such a way that the metal could be scraped, filed, or polished immediately after a low sensitiveness had been attained by heating, without removing from the tube or destroying the vacuum. At the time of this work it seemed to be too difficult from a mechanical standpoint. It seems now, however, that it should be less difficult if the platinum were used in the form of a wire rather than in the form of foil. It should be possible to draw a wire-drawing die or a sort of hollow, closely fitting file along the wire after it has been made relatively insensitive, remove the old surface, and form a new one of nearly gas-free platinum.

Does Mercury Vapour cause Low Sensitiveness when Heating at 100° *to* 500° *C.?*

When the photoelectric current from platinum is measured after heating at various increasing temperatures, one finds lower values in the interval of 100° C. to 500° C. Reference is made to figs. 3 and 4 of my previous paper *. The existence of this minimum has been confirmed by Herrmann †, who also noted its great persistence. The reader should note fig. 7 of his paper. He undertook to trace its origin, and concluded that it is very probably due to mercury vapour from the pumps. This conclusion is strongly supported by the curves 2, 3, and 5 of his fig. 8, these curves being obtained after the liquid air was removed from the trap, whereas all of the other curves which did not show the minimum were obtained when mercury vapour should be absent.

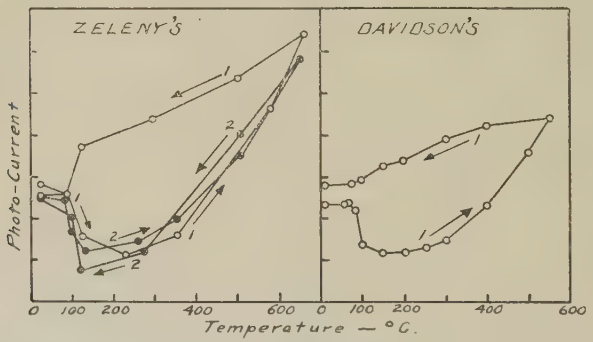
There are two circumstances, however, which must be considered before this explanation can be accepted. One is the fact that this minimum disappears when a run is made after the platinum has been heated for a sufficiently long time at a high enough temperature even if mercury

* *Loc. cit.* † *Loc. cit.*

vapour is permitted to be present. This is shown in fig. 5 of my previous paper *, and is also shown by Herrmann himself. Curve *d* of his fig. 7 is perfectly straight and horizontal, and he emphasizes the fact that no liquid air was used in all of his work shown in fig. 7.

The other circumstance is that this minimum appears in some early photoelectric experiments on platinum by Zeleny † and Davidson ‡. Their results are reproduced in fig. 4, the curves of Davidson being somewhat distorted as to scale. Their procedure was different from Herrmann's and from mine in that the photoelectric current was measured while the metal was hot. The significant thing for us, however,

Fig. 4.



Photoelectric current from platinum as function of temperature when heated in air at atmospheric pressure.

is that the experiments were conducted out in the open at atmospheric pressure and with apparatus which did not involve the presence of mercury. The only enclosures employed were those necessary for electrostatic shielding. It is clear then that the minima of the curves showing photoelectric sensitiveness as a function of heating-current or temperature of heating cannot be accounted for in the simple manner proposed by Herrmann. They disappear on long-continued high-temperature heating in spite of the presence of mercury vapour, and they are found with slightly used foils even when mercury vapour must be considered to be entirely absent.

* *Loc. cit.*
† *Loc. cit.*
‡ *Loc. cit.*

Some Experiments on the Influence of Gases.

After the sensitiveness of Foils Nos. 1 and 2 had been reduced to relatively low values, some experiments were made to test the influence of gases. Similar work was done with Foil No. 3 after the effect of scraping had been looked into. The results for all three foils are given in fig. 5. The runs are all consecutive, and the immediate previous treatments are described in the caption. It should be remembered that the previous maximum photoelectric current with Foil No. 2 was 299 scale-divisions, with Foil No. 3 it was 312 scale-divisions, and with Foil No. 1 it was over 400 scale-divisions. It is seen that in no case did treatment with gas fully restore the platinum to its previous maximum sensitiveness. It is noticed, too, that Foils Nos. 1 and 2 underwent no change after standing in a high vacuum, in hydrogen, in oxygen, or in the "condensable" gas. By condensable gas is meant that portion of the gas removed from the foil, or the surrounding parts of the tube, by heating, which had condensed in the liquid-air trap. It was released by removing the liquid-air. Foil No. 3 behaved differently. This foil regained sensitiveness on mere exposure to air or to the residual gases of low pressure within the tube. In one case this recovery was to nearly one-half of the previous maximum of 312 scale-divisions. The results of this section bring out again the influence of the particular sample of platinum on the results obtained in photoelectric work. Foils Nos. 1 and 2, which had been reduced in sensitiveness only with great difficulty, showed no tendency to recover on coming in contact with gases. Foil No. 3, however, which had been made insensitive very easily, recovered from a quarter to nearly half of its previous high sensitiveness on standing in air or in a high vacuum.

Heating the photoelectrically insensitive platinum to bright yellow glow in hydrogen, in oxygen, or in condensable gas changes its behaviour when it is subsequently carried through a series of increasing temperatures. The two runs made with Foil No. 2 after heating in condensable gas are in general agreement between themselves, as are also those made after heating the foil in hydrogen. These results of heating with hydrogen are in agreement with those of Herrmann * in that the maximum appears at the higher temperatures. It is not known whether or not this maximum sensitiveness could have been made to approach the previous

* *Loc. cit.*

Fig. 5.

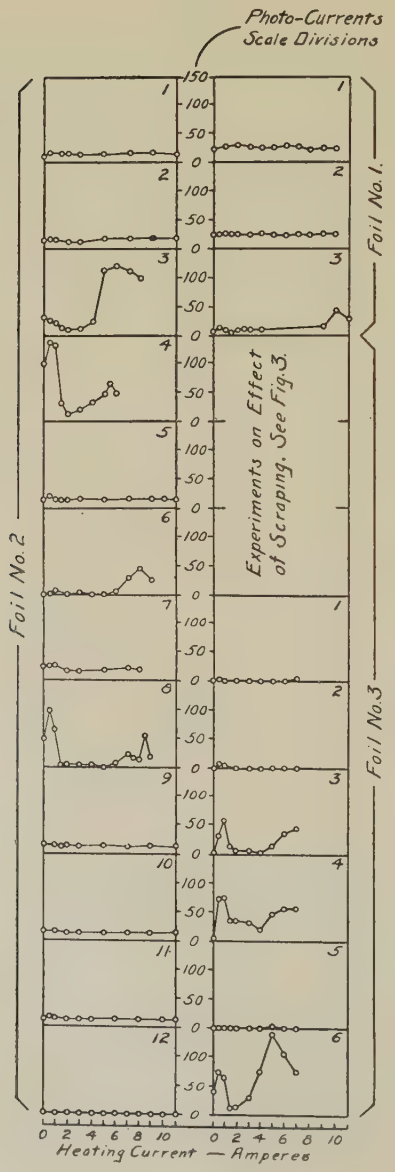


Photo-Currents
Scale Divisions
150
100
50
0
Foil No. 2
Foil No. 1.
Foil No. 3
Experiments on Effect of Scraping. See Fig. 3.
0 2 4 6 8 10
Heating Current — Amperes

Foil No. 2.—1. After standing in high vacuum 3 days following run No. 7, fig. 1.
2. „ standing in condensable gas 14 hours, pressure=2 mm.
3. „ heating in condensable gas, pressure=2 mm.
4. Immediately after preceding run.
5. After heating 70 minutes with 11 amperes, 1422° C.
6. „ „ in hydrogen, pressure=3 mm.
7. Immediately after preceding run.
8. After heating in condensable gas, pressure=1·5 mm.
9. Immediately after preceding run.
10. After heating 30 minutes with 10 amperes, 1380° C.
11. „ standing in oxygen 45 hours, pressure=10 cm.
12. „ heating in oxygen, pressure=3 mm.

Foil No. 1.—1. After heating 90 minutes with 11 amperes, 1416° C.
2. „ standing in hydrogen 48 hours, pressure=14 cm.
3. „ heating in hydrogen, pressure=12 cm.

Foil No. 3.—1. After heating 120 minutes with 7 amperes, 1140° C.
2. „ standing in air 2 hours, atmospheric pressure.
3. „ „ „ 8 days, „ „
4. „ „ in vacuum 1 day, then in air 4 days.
5. „ heating 105 minutes with 7 amperes, 1140° C.
6. „ standing in high vacuum 4 days.

maximum sensitiveness by choosing other pressures or other temperatures or times of heating. The results of heating in oxygen are also in agreement with Herrmann's results. After heating in this gas the sensitiveness remains low at all heating currents.

This experimental work was done during the spring of 1923 at the University of Wisconsin. I am indebted to Professor C. E. Mendenhall for the opportunity to do it and for valuable suggestions and criticism.

The Rockefeller Institute for Medical Research,
New York City, March 5, 1926.

XXXIX. *The Transference of Energy in Collisions between Electrons and Molecules.* *By* J. S. Townsend, *M.A., F.R.S., Wykeham Professor of Physics, Oxford, and* C. M. Focken, *B.Sc., Lincoln College, Oxford* *.

1. THE well-known electrical properties of gases which are observed in experiments on currents between two electrodes where potentials less than one hundred volts are used, have been the subject of many investigations, and suggestions have recently been made to account for the increase in conductivity with the force on certain hypotheses relating to the transference of energy from electrons to molecules which are said to be required by the quantum theory.

In these explanations of the conductivity no attempt is made to account for many of the principal features of the phenomena, and there is disagreement on many points with the results of the experiments.

It is of interest therefore to examine the experimental evidence which is usually quoted in support of the laws that have been adopted with regard to the transference of energy in quanta from electrons to molecules. This evidence seems to be very defective, and if the inquiry be extended to other experiments on the motion of electrons in gases at low pressures, the theory of the transfer of energy in quanta as it is generally stated is found to be quite untenable.

As the theory relates to a large extent to collisions in which electrons lose energy in amounts corresponding to resonance potentials, and large photo-electric effects which are supposed to result from the radiation from molecules, we have recently made some experiments with neon and helium in order to determine the relative importance of the photo-electric effect and the effect of ionization by collision in contributing to the conductivity of these gases. The results are the same as those which we obtained by other methods, but in the recent experiments a simpler form of apparatus was used which gives a more direct method of comparing the increases in conductivity resulting from these two processes.

2. The hypotheses relating to the transference of energy in quanta are described by Jeans † in his report on the quantum theory. In this report it is stated that the general

* Communicated by the Authors.

† J. H. Jeans, 'Report on Radiation and the Quantum Theory,' second edition, 1924.

truth of the ideas relating to the transference of energy from electrons to molecules is confirmed by experiments made by Franck and Hertz, and some of the results which were obtained with mercury vapour are quoted as examples of what may be expected to occur in general. The application of the quantum theory to the conductivity of gases is more fully described by Bloch *, and in his book on the subject special consideration is given to experiments exhibiting discontinuities in currents due to electrons moving under accelerating potentials. The principal hypotheses which have been adopted are the following :—

Electrons moving with small velocities rebound without any loss of energy whatever from atoms with which they collide,

As the velocity of the electron is increased a point is reached where the electron loses all its energy in a collision.

The only amounts of energy which an electron may lose in a collision are the precise amounts corresponding to resonance potentials or the ionizing potential.

These hypotheses, it will be noticed, are not in agreement with the principle of the conservation of momentum. The resonance potentials are comparatively large, being of the order of 10 volts, so that in many experiments the energy of each electron is less than that corresponding to a resonance potential of the gas. In these cases, if a molecule be supposed to be at rest before a collision, it is also at rest after the collision if the electron loses no energy, but the momentum of the system is changed owing to the change in the direction of motion of the electron.

3. With regard to the first hypothesis it may be stated that there are several experiments which show that electrons lose only a small proportion of their energy in collisions with molecules, but there are no experiments which show that the loss of energy is absolutely negligible in collisions where the direction of motion of the electrons is changed.

There are experiments which show that electrons lose some energy in these collisions, when the kinetic energy is large compared with the energy of agitation of the molecules. Collisions also do occur in which the electrons move almost exactly in the same direction before and after a collision, and in these cases the loss of energy is negligible in comparison with the loss in collisions where electrons are deflected. In

* L. Bloch, 'Ionization et resonance des Gaz et des Vapeurs,' 1925.

the following discussion we shall consider only the collisions in which the direction of motion of the electrons is changed.

The idea that electrons lose no energy in collisions with atoms is supposed to have been established by Franck and Hertz *, from measurements of velocities of electrons before and after collisions with molecules. A little consideration shows that the exact amount of energy which is lost in collisions cannot be found by this method. The difficulties enumerated by Bloch which occur in the determinations of critical potentials occur also in the measurements of the velocities before and after collisions. In helium, for example, a series of resonance potentials, V_1, V_2, etc. were obtained by Franck and Knipping †, which were considered to be in agreement with the formula $eV = k\nu$ giving the resonance potentials in terms of the frequencies ν of the spectral lines. The wave-lengths of these lines were subsequently determined by Lyman ‡, but the results he obtained were not in good agreement with the resonance potentials as found by Franck and Knipping. This discrepancy has shown that in estimating the correction for contact potential and the distribution of the velocities of the electrons an error amounting to 0·7 volt may occur in the absolute values of the resonance potentials. It seems very improbable that velocities can be measured by this method to an accuracy of one-tenth of a volt. The experiments with the smaller velocities may possibly be interpreted as showing that an electron does not lose more than about one per cent. of its energy in collisions with molecules, but they do not show that the loss of energy in a collision is absolutely negligible.

4. It may also be pointed out that another source of error may arise in the experiments on the loss of energy in collisions described by Bloch §, as the electric force is not zero in a gas contained in a metallic vessel when a stream of electrons from a filament is projected through a grid into the vessel. The space inside the vessel becomes negatively charged and there is a force towards the surface tending to increase the velocity of electrons which may move out through an aperture in the boundary. When a space with an equipotential boundary contains a gas at low pressure the space charge depends on the dimensions of the vessel

* J. Franck and G. Hertz, *Verh. d.D. Phys. Ges.* xvi. pp. 457, 512 (1914).

† J. Franck and P. Knipping, *Zeit. f. Phys.* i. p. 320 (1920).

‡ T. Lyman, 'Nature,' vol. cx. p. 278 (1922).

§ L. Bloch, *loc. cit.* p. 32.

and the intensity of the stream that enters it. This type of apparatus is used in several experiments, but the intensity of the stream of electrons which enters the space is not mentioned. As the smaller subsidiary currents are measured by a galvanometer the original filament emission would appear to be several microamperes. The following rough calculation indicates the order of the force which would be developed due to accumulation of charge in a vessel of ordinary dimensions if the rate at which the electrons reach the boundary were due to diffusion alone. In order to find the average time during which an electron may move about inside the vessel without touching the boundary, we may take the case of an electron at a point P at a mean distance of two centimetres from the boundary moving with a kinetic energy corresponding to three volts in helium at 2 millimetres pressure. If there be no loss of energy in collisions the kinetic energy remains constant, the velocity of the electron being 10^8 cm. per sec. The mean free path of the electron corresponding to this velocity is ·025 cm., so that the rate of change of the mean square of the distance R of the electron from the point P is obtained from the formula : $d\mathrm{R}^2/dt = 5 \times 10^6$. Thus the time required for the electron to reach the boundary is on an average 8×10^{-7} second. If a current of 10^{-5} ampere entered the space the total charge in the space at any instant would be $2{\cdot}4 \times 10^{-2}$ electrostatic unit, and if the boundary were a sphere of 2 centimetres radius the force at the surface would be 1·8 volts per centimetre.

If the electrons lose energy in collision with molecules, their velocity of agitation would be reduced, and there would be a corresponding increase in the force at the boundary. A considerable error may thus be made in treating the space inside a metal enclosure as a "force free" space, and in drawing conclusions from measurements of currents emerging from an aperture it is desirable to take into consideration the force due to the space charge.

5. The hypotheses relating to transference of energy in exact amounts involve other difficulties. They imply that the number of collisions in which electrons lose energy in amounts corresponding to resonance potentials is greater than the number of collisions in which molecules are ionized under some conditions where large increases of current due to ionization by collision are obtained. The question arises as to the probability of an electron losing an amount of energy equal to $e\mathrm{V}_1$, when its energy before the collision exceeds that amount : V_1 being a resonance potential.

The evidence on this point as obtained from experiments on mercury vapour, is very uncertain, and the results obtained by different observers are not in good agreement.

In an investigation by Franck and Einsporn *, on currents depending on the accelerating potential applied to electrons, there are fourteen points of discontinuity, in the curve representing the currents, obtained by changing the accelerating potential from 4 to 9 volts, giving fourteen resonance potentials between these two points. The curves seem to indicate that the probability of an electron losing energy in any of the critical amounts is small and is of the same order for each of the fourteen resonance potentials, but under these conditions sharp discontinuities in the current would not be expected.

Also, owing to the distribution of the velocities of the electrons emitted from the filament and the effect of the retarding field due to the space charge, the electrons collide with different velocities, so that even if there were critical amounts of energy characteristic of the molecules of the gas, abrupt changes in currents would not occur when the accelerating potential passes through these points.

A different result has been obtained by Foote and Mohler †, who found two critical potentials between 4 volts and 9 volts, which seems to indicate that electrons lose energy in a large proportion of collisions when they collide with molecules of mercury vapour with velocities corresponding to two of the critical potentials observed by Franck and Einsporn.

The theory has also been tested by investigations of another kind, where observations are made of the photo-electric effect due to the radiation emitted by molecules after absorbing energy in amounts equal to the quantities eV_1, eV_2, etc. In the experiments on this principle made by Richardson and Bazzoni ‡, a current from a filament was sent through mercury vapour, but no photo-electric effect was observed when the accelerating potential was less than 10·5 volts; also the photo-electric effect with larger accelerating potentials was very small compared with the current from the filament. This result is in accordance with those we have obtained from experiments with helium and neon, which showed that the photo-electric effect must be extremely small in comparison with the effect of ionization by collision.

* J. Franck and E. Einsporn, *Zeit. f. Phys.* ii. p. 18 (1920).

† P. D. Foote and F. L. Mohler, 'Origin of Spectra,' 1922.

‡ O. W. Richardson and C. B. Bazzoni, Phil. Mag. [6] xxxii. p. 437 (1916).

6. The transference of energy from electrons to molecules may be determined by a different method from the results of experiments on the motion of electrons in a uniform electric field.

In the initial stages of the motion of electrons which start with a small velocity, the kinetic energy of the electrons increases as they move in the direction of the electric force ; and since the direction of motion is changed in the collisions with molecules of the gas, the kinetic energy of the electrons appears as energy of agitation. After moving some distance in the direction of the force a steady state of motion is attained where the electrons lose energy in collisions with molecules at the rate at which they acquire energy by moving in the direction of the force. At this stage the motion of the electrons is represented by a mean velocity of agitation U and a mean velocity W in the direction of the force.

If it be supposed that the electrons lose no energy in collisions with molecules, until they attain the energy corresponding to the first resonance potential V_1, and then lose all their energy, they would again acquire the energy eV_1 after moving a further distance $z = V_1/Z$ in the direction of the force (Z). Thus the average energy of agitation of an electron when expressed in volts would be a certain fraction of the potential V_1. If AV_1 be the average energy, the coefficient A is independent of the electric force and pressure provided that the pressure is sufficiently great to ensure that each electron makes several collisions with molecules while its energy is slightly above the critical value V_1. The factor A depends on the velocity of an electron in the direction of the force during the time its energy of agitation rises from zero to V_1 : the value of A may thus be seen to exceed ·5, but for the purpose of this calculation this value may be attributed to A.

Under these conditions, if the first resonance potential in helium be taken to be 20 volts, the mean energy of agitation of electrons in the steady state of motion would be about 10 volts for any value of the electric force and any pressure of the gas. As no result of this kind has been obtained in the experiments on the determination of the values of U, it cannot be maintained that the electrons lose no energy except in amounts equal to eV_1.

7. The velocity of agitation U and the velocity W in the direction of the electric force have been determined for several gases over a wide range of electric force Z and gas

pressures p in the Electrical Laboratory, Oxford *. In all cases the velocities U and W were found to depend on the ratio of the electric force Z to the gas pressure p.

The energy of agitation may be expressed as the product of the atomic charge and a potential, and this potential may be taken as representing the kinetic energy of an electron moving with a velocity U.

In helium at 20 millimetres pressure the potential which represents the energy of agitation is ·42 volt when the electric force Z is 4 volts per centimetre. The energy of agitation increases when the pressure is reduced or the force increased. At 8 millimetres pressure the potential which represents the energy of agitation is 1 volt, with the same electric force of 4 volts per centimetre.

Thus not only is there a large change in the mean energy of agitation with the pressure, but also this energy is very much less than the energy corresponding to 10 volts.

8. The fact that the energy of agitation of electrons, moving under a small electric force, exceeds the energy of agitation of the molecules of the gas (which is approximately ·037 volt at 15° C.) shows that the electrons lose only a small proportion of their energy in collisions with molecules, as was pointed out when the first experiments † on the energy of agitation of electrons in air were made several years ago.

In order to determine the exact amount of energy lost in collisions it is necessary to find the velocity W in the direction of the electric force for the same forces and pressures as those used in finding the velocity of agitation. The proportion λ of the energy of an electron which is lost in a collision is thus obtained from the formula

$$\lambda = 2{\cdot}46 \times W^2/U^2.$$

For the range of values of the energy of agitation (from ·43 volt to 3·4 volts) the value of λ is approximately constant, and equal to $2{\cdot}5 \times 10^{-4}$ in helium.

Hence, even when the electrons lose only a very small proportion of their energies in collisions, this loss is sufficient to control the energy of agitation. This is due to the fact that the number of collisions per centimetre in the direction of the electric force (equal to U/Wl, where l is

* The results of the principal experiments, and tables of the velocities U and W are given in the pamphlet "Motion of Electrons in Gases," Clarendon Press, Oxford, 1925.

† Proc. Roy. Soc. A., lxxxi. p. 484 (1908).

the mean free path) is large since U is large compared with W.

As the electric force is increased values of the ratio Z/p are attained at which the effect of ionization by collision becomes appreciable, and for these values of the ratio Z/p there is a marked increase in λ. In the ordinary notation adopted to represent the rate of increase of currents due to ionization by collision the values of α/p are approximately ·04 and ·12 for the values of Z/p, 3 and 5 respectively, and the corresponding values of λ are $4{\cdot}15 \times 10^{-4}$ and $9{\cdot}8 \times 10^{-4}$.

It is important to notice that the change from the small values of λ, $2{\cdot}5 \times 10^{-4}$, to the large values as the force increases, is accompanied by the appearance of additional electrons due to ionization by collision. If there were large losses of energy in amounts corresponding to resonance potentials which are smaller than the ionization potentials, increases in the value of λ would have been observed before ionization by collision became appreciable, and no effect of ionization by collision would have been observed with values of Z/p as small as 3 or 5.

It may be mentioned that the energy required to ionize a molecule cannot be obtained from the rate of increase of λ with the force by simple calculation. When new electrons are generated in the gas the quantity $2{\cdot}46W^2/U^2$ does not accurately represent the average loss of energy of an electron in a collision. When an electron loses a large proportion of its energy the value of U is reduced, but if in addition a new electron is set free from a molecule with a small initial energy of agitation, a further reduction in the average value of U occurs owing to the increase in the number of electrons with small kinetic energy. In consequence of these two effects there is a large increase in the ratio W^2/U^2 when ionization becomes appreciable.

9. Bloch suggests that the conclusions which have been drawn from these experiments with regard to the values of λ and variations of the mean free path L are unreliable, since the formulæ connecting λ and L with the velocities U and W which are used are obtained on the classical principles of mechanics, and large losses of energy in amounts corresponding to resonance potentials are not considered.

As the experiments do not lead to any conclusion which is contrary to the principles involved in determining these formulæ, and as the values of the energy of agitation found experimentally are completely different from the value

indicated by the theory of transference of energy in quanta, it would be unreasonable to adopt the latter theory.

In the kinetic theory of gases in its classical form as applied to the motion of electrons in gases, it is not necessary to assume that the mean free path or the mobility is constant. In fact, if the mean free path of an electron be supposed to be constant, the mobility must change with the electric force. The formula connecting the velocity W in the direction of the electric force with the mean free path may be written

$$W = \frac{Z}{p} \times \frac{eL}{m\overline{U}} \times \cdot 815,$$

where p is the gas pressure, and L the mean free path at 1 millimetre pressure.

In this case, where the electrons move under a uniform electric force, the only difficulty in obtaining the formula occurs in determining the distribution of the velocities about the mean, as the numerical constant depends on this distribution. But the constants found by assuming different distributions are not much different from the value ·815, which is the number obtained on the hypothesis that the velocities are distributed according to Maxwell's law. Whatever be the correct value of the numerical constant, the mobility, which is proportional to $\frac{e}{m} \times \frac{L}{U}$, must diminish as U increases. Thus, as the theory requires that U should increase with the ratio Z/p, it also requires that the mobility should diminish as Z/p increases.

10. The velocities W as found experimentally confirm this conclusion in so far as it has been found that W does not increase directly as the electric force or inversely as the gas pressure.

The quantity $W.U.p/Z$ is not constant, which shows that the mean free path varies with the velocity of agitation. When this result was first obtained * in the experiments on the motion of electrons in air, it was pointed out that collisions between electrons and molecules cannot be supposed to be analogous to collisions between elastic spheres. This analogy implies that in a collision with a molecule at rest the deflexion of an electron is independent of the velocity of the electron. Also, with spheres, the mean free path is a constant independent of the velocity of the electron, as it

* J. S. Townsend and H. T. Tizard, Proc. Roy. Soc. A. vol. lxxxviii. (1913).

represents the average distance traversed by an electron between two consecutive contacts with spheres of fixed radii.

In the formula for W the shape of the molecules is not considered, the length L being defined as the average distance an electron moves in a given direction with the velocity U before all directions of motion become equally probable, when the electric force Z is zero. In all cases the length L changes with the velocity of agitation, and in most cases, as in air, L increases as U diminishes for a large range of values of U.

11. There are also remarkable discrepancies between the conclusions drawn by German physicists from experiments on the performance of electrons in diatomic gases contained within an equipotential boundary where the space is said to be "force free," and the properties of these gases which may be deduced from the determinations of the motion of electrons in a uniform electric field.

The former experiments have been interpreted as showing that the loss of energy of electrons in collisions with molecules of oxygen is much greater than the loss with molecules of nitrogen or hydrogen, and it has been concluded that molecules of oxygen, and other electronegative gases, are surrounded by an intense electric field extending to a considerable distance which exercises an attractive force on electrons *. The only force of this kind which is recognized in ordinary mechanics is the force due to an electric charge, but as it cannot be supposed that molecules of oxygen in their normal state are positively charged, the above statement implies that there is an attractive force on electrons which constitutes a special property of molecules of oxygen.

If there were any field of force surrounding a molecule of oxygen much stronger than the fields of force surrounding molecules of nitrogen or hydrogen, the mean free paths of electrons would be shorter in oxygen than in these two gases. A comparison of the mean free paths in these gases, as deduced from the values of U and W, shows that it is in hydrogen that the free paths are the shortest.

Usually it is assumed that in the electric field surrounding a molecule the force repels electrons in some parts of the field and attracts electrons in other parts, the normal induction through a closed surface surrounding the molecule being zero. The intensity and distribution of the force in this field depends on the number and positions of the

* L. Bloch, *loc. cit.* pp. 17, 33.

electrons in the molecule. When the number of electrons is small the force in the external field may be greater than when the number is large.

The values L depend on the velocity U, but for a large range of values of U, from 3×10^7 to $1{\cdot}2\times10^8$ cm. per sec., the free paths are longer in oxygen than in nitrogen or hydrogen. The following are the mean free paths of electrons moving with a velocity of agitation 6×10^7 cm. per sec., in these gases at one millimetre pressure: in oxygen * L=·057 cm., in nitrogen L=·029 cm., in hydrogen L=·0215 cm.

Thus the longer free paths are obtained in the gases of large atomic weight. It is interesting to observe that a similar result was obtained with monatomic gases. The velocities U and W have been determined for three monatomic gases, and the following are the mean free paths at a millimetre pressure corresponding to the velocity of agitation $U=6\times10^7$: in argon L=·75 cm., in neon L=·21 cm., in helium L=·048 cm.

The large values of L show that in many collisions with molecules the direction of motion of the electron is very nearly the same before and after the collision, and it is to these collisions that we refer in section 3 in stating that the loss of energy is negligible. In equating the average loss of energy λ to the quantity $2{\cdot}46\,.\,W^2/U^2$, collisions of this type are left out of consideration and the total number of collisions per second of each electron is taken as U/L.

12. The experiments on the measurements of the velocities U and W show that the motion of electrons through a gas is completely controlled by the losses of energy in small amounts when the electric forces are small, so that when the forces are increased and ionization by collision begins to appear the losses in the smaller amounts cannot be left out of consideration. The simplest experiments on the effect of ionization by collision are those where electrons move between two parallel plates and the currents are measured with different potentials between the electrodes. A supply of electrons may be obtained by the action of ultra-violet light on the negative electrode, or from a filament, which may be situated near the negative electrode or in the plane of the negative electrode and the mean potential of the filament maintained at the same potential as that of the negative electrode.

* The value of L for oxygen is taken from Brose's recent experiments with that gas. H. L. Brose, Phil. Mag. i. p. 536, Sept. 1925.

The number of electrons that pass from the negative electrode, or from the filament, to the positive electrode increases with the potential difference between the electrodes, but for certain values of this potential there are large increases in the current between the electrodes which are generally attributed to ionization by collision. Usually the increase of current due to this cause has been found to be so gradual that it is impossible to determine the exact point at which a definite effect of ionization by collision begins to appear, but according to Franck and Hertz * there is an abrupt increase of current in helium when the potential difference between the plates is 20 volts and in neon when the potential difference is 16 volts.

According to the original interpretation of these and other experiments made by Franck and Hertz†, the electrons lose no energy in collisions with molecules of the gas until they attain the energy required to ionize a molecule, and immediately the electrons acquire that amount of energy they ionize the molecules with which they collide. The potentials 20 ‡ volts and 16 volts were therefore said to be the ionizing potentials in these gases.

From our point of view these numbers represent upper limits of the ionizing potentials, as it has been shown that electrons lose some energy in collisions before they acquire sufficient energy to ionize molecules, and there is no reason for supposing that an appreciable proportion of the electrons ionize molecules when they attain the exact amount of energy which represents the work done in separating an electron from a molecule.

13. According to the quantum theory of the transference of energy in its more recent developments, electrons lose energy in collisions with molecules in amounts proportional to the frequency of certain spectral lines. These amounts may be expressed in potentials V by the formula $eV = h\nu$, where e is the atomic charge, h Planck's constant, and ν the frequency of the spectral line.

Thus the resonance potentials V_1, V_2, etc. are found accurately from measurements of spectral lines. According to the theory the resonance potentials are less than the ionizing potential, so that if a large proportion of the electrons lose energy in amounts corresponding to resonance potentials, the effect of ionization by collision would be very

* J. Franck and G. Hertz, *Verh. d. D. Phys. Ges.* xv. p. 929 (1913).

† J. Franck & G. Hertz, *Phys. Zeits.* xvii. p. 430, 1916.

‡ The number 20·5 appears in some tables.

small in many experiments where large increases in current have been found to be due to that process of ionization. It is necessary therefore to suppose that in some gases losses of energy in amounts corresponding to resonance potentials occur only in a very small proportion of the total number of collisions in which the energy of the electron exceeds those amounts.

But the principal difficulty in connexion with the theory is that in some gases the resonance potentials, as determined from the wave-lengths of the spectral lines, are greater than the ionizing potentials which were determined experimentally. From Lyman's recent measurements of wave-lengths * the lowest resonance potential in helium is found to be 20·55 volts and the greatest 24·55 volts, the latter according to the theory being the ionizing potential.

In order to meet these difficulties other experiments were made from which it has been concluded that the ionizing potential in helium is about 25 volts, and the increase in current which occurs at lower potentials is said to be due to a photo-electric effect. Similarly in neon the ionizing potential in that gas is now supposed to be 21·5 volts instead of 16 volts.

If these conclusions be correct, it is remarkable that in Franck's earlier experiments an abrupt increase of current was not observed in helium at the point where the potential difference between the electrodes was 25 volts or in neon at 21·5 volts, especially as it is claimed that critical potentials may be determined by discontinuities in currents even when the gas contains small quantities of impurities.

14. In the original investigations which were made in connexion with the theory of ionization by collision, the conductivity of a gas between parallel plates was examined very carefully, and it was found that the experiments were accurately explained on the hypothesis that the increases in the currents were due to ionization of molecules of the gas by collisions with electrons.

No other process of ionization has since then been suggested which gives a consistent explanation of the principal experiments on the conductivity between parallel plates.

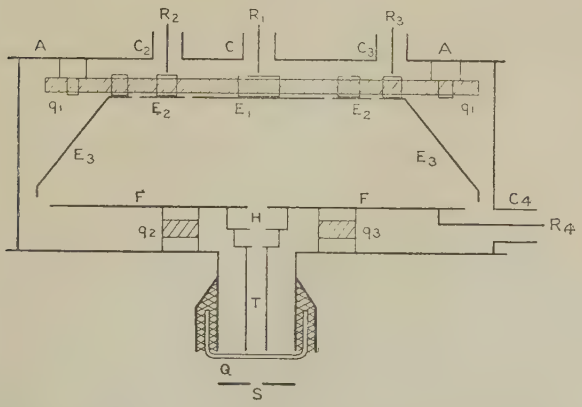
The question arises as to whether any appreciable part of the increases in currents obtained by increasing the potential between the plates may be attributed to a photo-electric effect.

* T. Lyman, *loc. cit.*

The experiments which have hitherto been made to detect a photo-electric effect of radiation due to small currents in a gas, have shown that there is no photo-electric effect which is comparable with the effect of ionization by collision. This result was obtained by Gill* in experiments with air in which the initial supply of electrons was obtained by ultra-violet light. A similar result was obtained by a different method for currents in helium †, neon, nitrogen, and hydrogen ‡, where the initial supply of electrons was obtained from a filament in the space between two parallel plates. In these methods of investigation a photo-electric effect would have been indicated by the difference between two currents, so that a small effect comparable with the experimental error in the measurement of a current might have escaped observation.

As the question is of importance from a theoretical point of view, it was considered desirable to make another investi-

Fig. 1



gation by a method in which the electrodes are arranged so that a small photo-electric effect would be indicated more directly.

15. In the investigations which have recently been made the apparatus was arranged as shown in fig. 1. The electrodes were symmetrical about the line joining the centres of the plate electrodes E_1 and F, and the figure represents a section of the apparatus through this line. The large electrode F was charged positively and attracted the electrons liberated from the electrode E_1 by a narrow beam

* E. W. B. Gill, Phil. Mag. xliii. p. 852, Nov. 1921.

† J. S. Townsend and S. P. McCallum, Phil. Mag. [6] xlvii. p. 737 (1924).

‡ S. P. McCallum and C. M. Focken, Phil. Mag. [6] xlix. p. 1309 (1925).

of ultra-violet light. The light, emitted from the spark-gap S, entered the apparatus through a quartz window Q and passed through a long metal tube T attached to the lower plate F. The quartz window was sealed to a short length of tubing which dipped into a metal channel, where it was sealed in with lead. The aperture H in the plate F through which the light passed was 5 millimetres in diameter, so that nearly all the light entering the apparatus fell on a small area at the centre of the disk E_1. A ring electrode E_2 of internal diameter 3·5 centimetres and external diameter 6 centimetres was fixed in the same plane as the disk E_1. The diameter of the disk was 3·3 centimetres, which allowed a space one millimetre wide between the disk and the ring for insulation. A third electrode E_3, shaped as shown in the figure, extended from the plane of the electrodes E_1 and E_2 to the plane of the lower plate F. The electrode E_3 was insulated from E_2 by a narrow space one millimetre wide, and from the electrode F by a larger distance.

The electrodes E_1, E_2, and E_3 were mounted on a quartz rod q_1 of rectangular section, which was fixed at the ends

Fig. 2.

to the upper plate A of the case. The electrode F was similarly mounted on two narrow quartz rods, q_2, q_3, fixed to the lower plate B of the case.

Connexion to the electrodes was made by the rods R_1, R_2, R_3, and R_4, which passed through long glass tubes G, as shown in fig. 2. The glass tubes were sealed at both ends to copper tubes C and D, and the rods R were soldered to disks which closed the ends of the tubes D. The tubes C were soldered to the case of the instrument in the positions C_1, C_2, C_3, and C_4, shown in fig. 1. A copper glass seal was also used for connecting the glass tubing which led from the apparatus to the pressure gauge and the charcoal tubes in which the gases were purified. All the electrodes and the metal case of the instrument were of brass which was silver-plated.

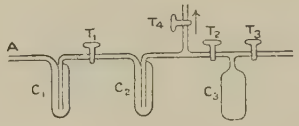
16. Thus the whole apparatus was made up entirely of glass, quartz, and metal parts, and it was possible to heat it up to a temperature of about 100° C. to expel gas from the

metal surfaces. The temperature was limited by the melting-point of the soft solder which it was necessary to use in connecting the tubes C to the case. After exhausting the apparatus and heating it for several hours there was found to be a very small leak in the case, but it was made absolutely air-tight by covering the soldered junctions on the outside with a hard wax cement.

Any remaining trace of impurity in the apparatus was removed by washing it out with some of the pure gas, and when this was done, the effect of impurities from the metal surfaces was so small that no change was observed in the electrical properties of the gas after keeping it in the apparatus for several days.

The gases used were helium and neon, from which nearly all impurities may be removed by charcoal cooled with liquid air. In order to make sure that the gases were free from hydrogen, they were introduced into a glass vessel with oxygen obtained by electrolysis of barium hydrate, and a discharge was passed through the mixture for about

Fig. 3.



twenty hours. The vessel contained phosphorus pentoxide to absorb any water vapour which might be formed. The gas was then passed slowly over copper-foil heated in quartz tubes, to remove the oxygen, and from these tubes it was admitted into a tube containing charcoal cooled with liquid air. The gas was then pumped into flasks with mercury-sealed taps. Most of this work was done by Mr. McCallum, as he also required some of these gases for experiments which will be described in another paper.

The neon used in these experiments was given to us by M. Georges Claude. The only impurity in it was a small quantity of helium, probably less than one per cent. of the neon.

The apparatus shown in fig. 1 was connected to the tube A, fig. 3, leading through small charcoal tubes C_1 and C_2 to the large charcoal tube C_3 with mercury-sealed taps T_2 and T_3 on either side. The apparatus was exhausted through the tap T_4 which led to the mercury gauge and the pump. Gas from the containing flask was admitted to the tube C_3 to a

pressure of about 300 millimetres, and the three charcoal tubes were cooled with liquid air for about twelve hours before the gas used in an experiment was admitted to the apparatus. The space between the taps T_1, T_2, and T_4 was used for taking small quantities of gas from the large tube C_3.

In order that no mercury vapour from the gauge should get into the apparatus while taking the pressure, the pressure in the gauge was reduced before opening the tap T_4. Thus the stream of gas always went in the direction of the arrow through the tap T_4.

17. The dimensions and positions of the electrodes were determined by the following considerations. The electrodes E_1, E_2, and E_3 were at zero potential throughout, and F at a positive potential V, so that when the beam of ultra-violet light from S falls on E_1, the electrodes E_2 and E_3 may acquire positive charges, by positive ions arriving from the gas or by the escape of negative electricity due to the photo-electric effect of radiation from the gas. The principal current flows from E_1 to F. The stream of electrons set free from the centre of E_1 diverges and falls on a large area of the electrode F. When the potential V is increased molecules of gas are ionized, and the positive ions received by E_1 are distributed over a much wider area than that from which the electrons were set free. The diameter of E_1 was determined so that in helium nearly all the positive ions should fall on this electrode for considerable ranges of the electric forces and gas pressures. An approximate estimate of the minimum diameter which would satisfy this condition was obtained from the results of the experiments on the divergence of streams of electrons in helium. The diameter 3·3 cm. may appear to be too small as the distance between the electrodes is 2·55 cm., but in these experiments the electrons start from the negative electrode with very small kinetic energy, and with the smaller forces they do not acquire the energy of agitation of the steady motion corresponding to the electric force until they have traversed a considerable part of the distance between the electrodes. In the first part of the path the lateral diffusion of the stream is therefore comparatively small, and in the neighbourhood of the electrode F, the electrons are not so widely distributed as they are in the experiments where they pass through a slit in the negative electrode with the energy of agitation of the steady motion corresponding to the electric force.

The divergence of the stream increases as the pressure is reduced and is greater in neon than in helium, so that in

helium at the lower pressures some of the positive ions are received on the ring electrode E_2, and in neon they may extend to both electrodes E_2 and E_3.

The solid angles subtended by the electrodes E_1, E_2, and E_3 at the centre of the plate F are $2\pi \times \cdot 17$, $2\pi \times \cdot 19$, and $2\pi \times \cdot 64$ respectively, so that if radiation were given out uniformly in all directions from the centre of the plate F, these numbers represent the proportion in which the energy would be received by the three electrodes. In the initial stages of the development of large currents, radiation from the gas due to collisions of electrons with molecules would come from points near the electrode F, and the number of electrons it would set free from the three electrodes would be approximately proportional to the above numbers. Thus about the same number would be set free from the disk E_1 and the ring electrode E_2, and about three times as many from the large electrode E_3.

18. Let n_1, n_2, and n_3 be the currents to the three electrodes, and N_1 the current comprising the electrons set free from the centre of the disk E_1 by the beam of ultra-violet light from the spark-gap S. The quantity N_1 increases with the electric force and it cannot be found accurately by these experiments. The ratio n_1/N_1 for several values of the potential V has been found by other experiments, but for the purpose of this investigation it is unnecessary to obtain the exact value of N_1.

If the increase of current $(n_1 - N_1)$ be due to ionization of the gas by collisions of electrons with molecules in the path of the original stream N_1, then $(n_1 - N_1)$ would be large compared with n_2 or n_3.

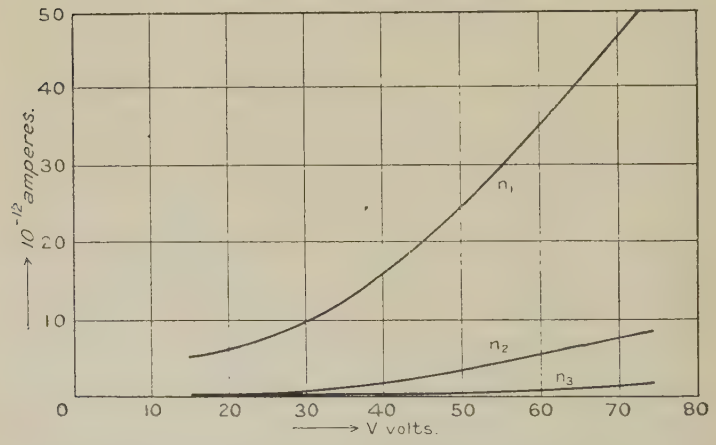
If the increase of current $(n_1 - N_1)$ be due to a photo-electric effect of radiation from the gas then $(n_1 - N_1)$ would be approximately equal to n_2, and n would be about three times as great as $(n_1 - N_1)$ or n_2.

The currents n_1, n_2, and n_3 to the electrodes were determined with the plate F at various potentials from 16 to 80 volts, for different gas pressures. The currents were measured by an induction balance, using a sensitive electrometer as an indicator. By this method the potential of the electrode does not vary more than one-tenth of a volt from the zero potential during the course of a measurement. In all cases the current n_3 was found to be small compared with n_1, and it is clear that in helium 99 per cent. of the increase of current $(n_1 - N_1)$ for the range of potentials used must be due to ionization of molecules of the gas by collisions with electrons.

In neon it is not possible to obtain an upper limit of the effect of radiation as accurately as in helium, but it may be seen that it does not exceed 5 per cent. of the effect of ionization by collision.

The experiments with helium were made at pressures of 2, 4, 8, and 16 millimetres. The increase of current with the potential V was greater at 4 millimetres pressure than at the other pressures. At 16 millimetres the increase of current was comparatively small. The currents obtained at the pressure 2 mm. are given by the curves fig. 4, and those at 8 mm. by the curves fig. 5. The ordinates of the curves n_1, n_2, and n_3 are the currents to the three electrodes, the abscissæ being the potentials of the electrode F in volts.

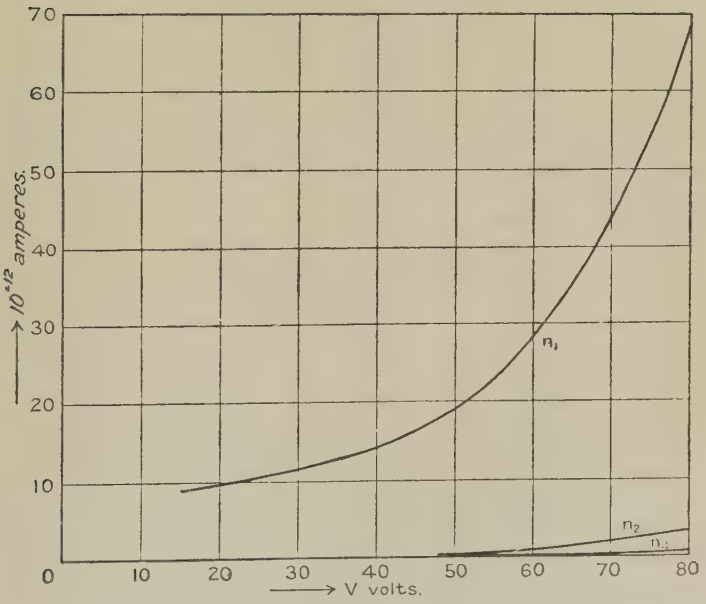
Fig. 4.—Helium. $p=2$ mm.



The principal difference between the results obtained at these two pressures is in the current n_2 to the ring electrode. At the lower pressure the stream of electrons from E_1 is so divergent that a larger proportion of positive ions are received on the electrode E_2. At 2 millimetres pressure the current n_1 is about twice the current N_1 at the potential $V=45$ volts, as found by other experiments, so that in the units in which the currents are given (n_1-N_1) is 10. Most of the small current n_3 is due to electrons set free from the electrode E_3 by scattered light from the original beam, since a current to this electrode is obtained when V is 16 volts. Like the main current n_1, the small current n_3 increases with the potential V. At the point $V=16$ the

current n_3 is about ·12, and at V=45 about ·55. The current at the latter potential to be expected from the normal increase of the current ·12 is about ·5. Hence at the point V=45 volts the current to the electrode E_3, which may be attributed to radiation from molecules of the gas, cannot exceed ·1, and one-third of this amount represents the effect which radiation from molecules of the gas may have at the electrode E_1. Thus the photo-electric effect due to radiation from molecules of the gas cannot be as much as one per cent. of the effect of ionization by collision in increasing the current n_1.

Fig. 5.—Helium. p=8 mm.



At the higher pressures the effect of radiation from molecules of the gas is even less than at 2 millimetres.

The results of the experiments with helium at 4 millimetres pressure are given by the figures in Table I., as the currents cannot be compared very accurately by the curves. The potentials V are given in volts, and the unit of current is 10^{-12} ampere.

Experiments were also made with neon at the pressures 2, 4, 8, and 16 millimetres. In this gas the effect of change of pressure on the conductivity is not so great as in helium.

Also the effect of lateral divergence due to diffusion is greater than in helium, as is shown by the comparatively large current n_2 to the ring electrode E_2, which at the lower pressures was as great at 14 per cent. of the total current. The best conductivity was obtained with the gas at 16 milli-

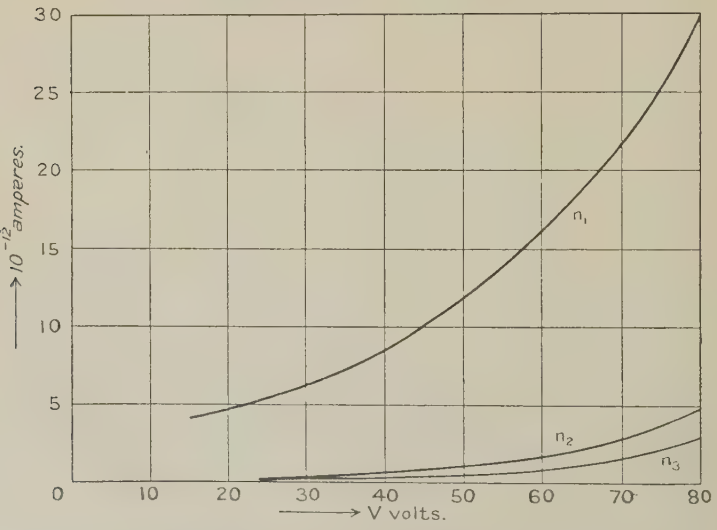
TABLE I.

Helium, 4 mm. pressure.

V.....	16	30	40	48	60	72
$\frac{X}{p}$	1·57	2·94	3·92	4·71	5·9	7·1
n_1	6·4	10·1	16·5	22·8	41·2	58·2
n_2	—	·10	·94	1·9	4·8	7·23
n_3	·08	·11	·21	·32	·62	·90

metres pressure, and the currents n_1, n_2, and n_3 for this pressure are represented in terms of the potential V by the curves fig. 6.

Fig. 6.—Neon, $p=16$ mm.



In this gas, although an increase in current due to ionization by collision is more marked than in helium when the potential V is 20 volts, a potential larger than 45 volts

is required to double the initial current N_1. At the potential 55 volts n_1 is about double N_1, so that at this point of the curve $(n_1 - N_1)$ is 7 units, and n_3 is ·7 unit.

As the current n_3 is an upper limit to the photo-electric effect on the electrode E_3 due to radiation from the gas, one-third of this current is an upper limit to the effect of radiation from the gas on the electrode E_1. So that this effect is less than 5 per cent. of the effect of ionization by collision in the increase of the current n_1. At the point $V = 55$ volts the current n_2 is 1·4, and n_3 is ·7. The part of the current n_2 due to positive ions generated by the stream N_1 is approximately $\left(n_2 - \frac{n_3}{3}\right) = 1{\cdot}2$, which indicates a very wide distribution of the positive ions. Consequently a part of the current n_3 must be attributed to positive ions, and the actual value of the photo-electric effect may be considerably below the upper limit given above.

The results of the experiments with neon at 8 millimetres pressure are given by the figures in Table II., the units of potential and current being the same as in Table I.

TABLE II.

Neon, 8 mm. pressure.

V.....	24	48	60	72	80
$\frac{X}{p}$	1·18	2·36	2·94	3·53	3·92
n_1	5·3	11·0	15·6	20·9	25·3
n_2	·24	1·31	2·04	3·04	4·28
n_3	·12	·69	1·27	2·08	3·08

The following conclusions may therefore be drawn from these and other experiments on the conductivity between parallel plates. A definite increase in current due to ionization by collisions may be obtained in helium with potentials as low as 21 volts and in neon with potentials as low as 17 volts. These numbers are upper limits of the ionizing potentials. The increase of current which may be attributed to a photo-electric effect of radiation from molecules of the gas is small compared with the increase of current due to ionization by collision.

XL. *Notices respecting New Books.*

Summation of Series. By L. B. W. Jolly, M.A. (Chapman & Hall. 13*s.* 6*d.*)

THE author has made a very extensive collection of results from various mathematical sources, commencing with the simple progressions and the sums of powers and products of natural numbers. It is interesting to note in this connexion that the values of some oscillating series, *e. g.* $1-3+6-10+\ldots\ldots\infty$, are given; the summation is easily made by the method of differences. An extreme example of this character occurs on page 164, where Euler's value of the series $1!-2!+3!-4!+\ldots\ldots\infty$ is given as calculated from a continued fraction. Further series are related to the exponential and logarithmic functions and other power series, in some of which the numbers of Bernouilli and Euler appear. Nearly half the book is devoted to trigonometrical and hyperbolic summation, which should be of use in the solution of various technical problems. A passing reference is given to the Gamma, Elliptic, Bessel and other functions. Blank pages are left for the insertion of further results. The bibliography gives a list of the authorities consulted in the preparation of this valuable collection.

Four-figure Mathematical Tables. Kaye and Laby. (Longmans Green & Co. 1*s.*)

A useful and inexpensive set of logarithmic and other tables. In addition to the ordinary tables of logarithms to four and five places, the series includes tables of the natural trigonometric functions with their logarithms, reciprocals and squares, and a table for the conversion of degrees of angles to radian measure. Values of some of the simple functions of π and e are also given with the logarithms to five places of decimals.

The Nervous Mechanism of Plants. By Sir Jagadis Chunder Bose. (Longmans, Green & Co. 1926. 16*s.* net.)

Sir J. C. Bose has done important pioneer work in scientific biology, and the present volume gives a further instalment of the researches which he is carrying on at the Bose Institute, Calcutta. The results of his investigations during the last twenty-five years tend to establish the theory that the physiological mechanism of the plant is identical with that of the animal. In the present work it is shown that not only has a nervous system been evolved by the plant, but that it has reached a very high degree of perfection, as marked by the reflex arc in which a sensory becomes transformed into a motor impulse. There is no doubt that the broader outlook which regards physiological mechanism as one unified class of problems whether they belong to plants or animals will lead to a great advance in physiological research and our knowledge of the irritability of all living tissue.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]

A. Phosphor-Bronze Strip (unannealed).
[Shows marked variation of rigidity.]

B. Phosphor-Bronze Strip (annealed).
[Shows only slight variation of rigidity.]